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Electrochemical Society

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CONTENTS

Editorial

Flood Control 265C

Technical Papers

The Electrochemical Behavior, Including Hydrogen Overvoltage, of Iron in Acid Environments. *Milton Stern* 609
Some Properties of Tin(II) Sulfate Solutions and Their Role in Electrodeposition of Tin, III. Solutions with Tin(II) Sulfate, Sulfuric Acid, and Addition Agents. *C. A. Discher* .. 617
Separations with a Mercury Electrode; Determination of Certain Metallic Impurities in Vanadium Salts. *William E. Schmidt and Clark E. Bricker* 623
Magnesium Fluorosilicate Phosphors. *P. W. Ranby and S. T. Henderson* 631
Investigations of Surface Recombination Velocities on Germanium by the Photoelectromagnetic Method. *T. M. Buck and W. H. Brattain* 636
Electrodeposition of Titanium on Base Metals. *M. E. Sibert and M. A. Steinberg* 641
Liquidus Curves for Aluminum Cell Electrolyte, I. Cryolite-Alumina. *N. W. F. Phillips, R. H. Singleton, and E. A. Hollingshead* 648
The Vapor Pressure of Rhenium. *E. M. Sherwood, D. M. Rosenbaum, J. M. Blocher, Jr., and I. E. Campbell* 650
The Kinetics of Formation of Anodic Ta_2O_5—Further Studies. *D. A. Vermilyea* 655

Technical Note

Surface Contamination of Copper by Phosphate Ion during Electropolishing—Use of P^{32}. *N. H. Simpson and Norman Hackerman* 660

Current Affairs

News Notes in the Electrochemical Field 267C
Division News 269C
Section News 270C
New Members 270C
ECS Membership Statistics 270C
Personals 271C
Meetings of Other Organizations 272C
Announcements from Publishers 274C
Employment Situations 274C
Literature from Industry
New Products

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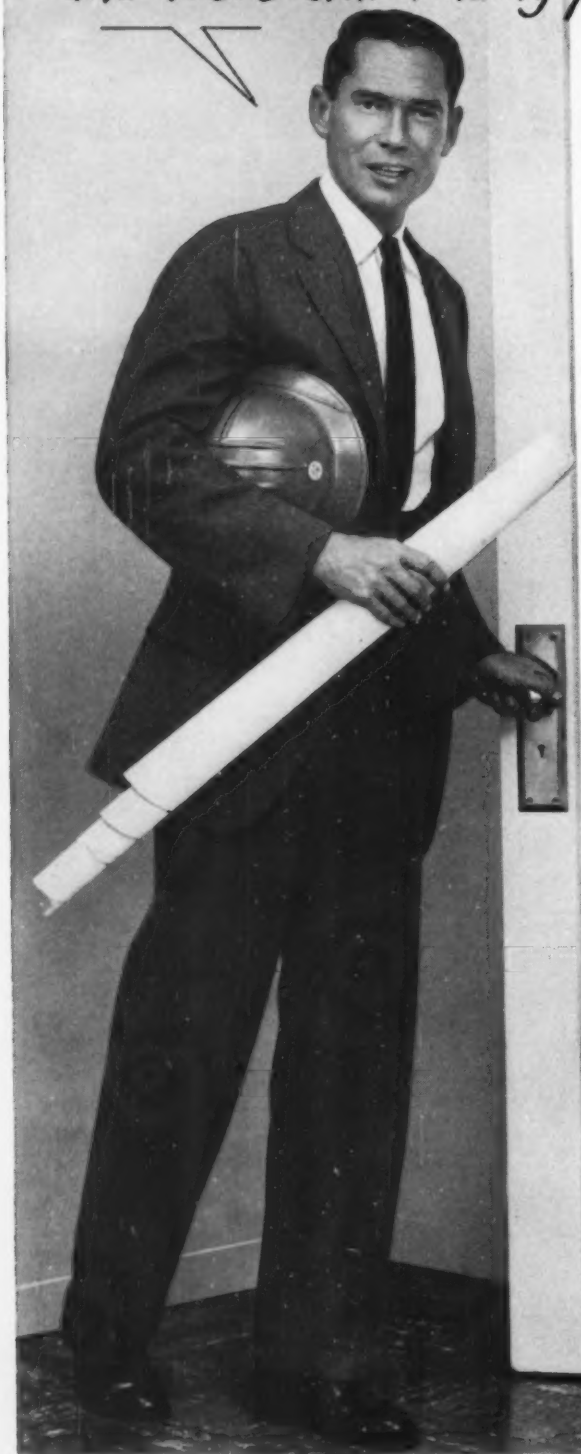

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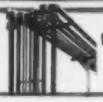

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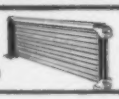

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Developed and sponsored by The Electrochemical Society, Inc., this definitive series of books is part of a comprehensive program intended to provide chemists, metallurgists, chemical and other engineers, ceramicists, and others with a useful background in modern electrochemistry and its related fields. It is also intended to spur research in the application of electrochemical techniques. Check these titles . . .

MODERN ELECTROPLATING

Edited by ALLEN G. GRAY, *Steel Magazine*. Draws on the experience of 39 top-level experts to provide a complete one-volume summary of current industrial electroplating practice. "A must for the metal finisher's library." — *Metal Finishing*. 1953. 563 pages. $9.50.

ELECTROCHEMISTRY IN BIOLOGY AND MEDICINE

Edited by THEODORE SHEDLOVSKY, Rockefeller Institute for Medical Research. Based on a symposium at The Electrochemical Society, this is a comprehensive discussion of current work indicating the trend of modern thinking and highlighting various aspects of research. 1955. 369 pages. $10.50.

VAPOR-PLATING

The Formation of Metallic and Refractory Coatings by Vapor Deposition

By C. F. POWELL, I. E. CAMPBELL, and B. W. GONSER, all of the Battelle Memorial Institute. The first single source of reference data on applications and techniques of vapor deposition. 1955. 158 pages. $5.50.

CORROSION HANDBOOK

Edited by HERBERT H. UHLIG, Massachusetts Institute of Technology. Authoritative, condensed discussions of virtually all aspects of corrosion in practically every type of metal and alloy. ". . . a historic contribution to corrosion literature." — *Chemical Engineering*. 1948. 1188 pages. $15.00.

ABSTRACTS OF THE LITERATURE ON SEMICONDUCTING AND LUMINESCENT MATERIALS AND THEIR APPLICATIONS

Compiled by the BATTELLE MEMORIAL INSTITUTE. An annual series collecting literature references to semiconducting and luminescent materials in technical and scientific publications. *1953 Issue*: 1955. 169 pages. $5.00. *1954. Issue*: In Press. Probably $5.00.

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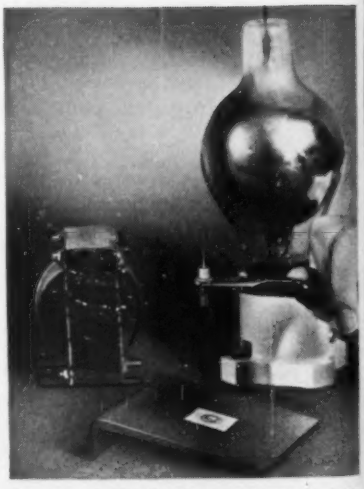
A GIANT FOR ITS SIZE!

Telephone science produces an important new rectifier

At Bell Laboratories one line of research is often fruitful in many fields. Latest example is the silicon power rectifier shown above.

Product of original work with semiconductors—which earlier created the transistor and the Bell Solar Battery—the new rectifier greatly reduces the size of equipment needed to produce large direct currents. It is much smaller than a tube rectifier of equal performance and it does not require the bulky cooling equipment of other metallic rectifiers.

In the Bell System the new rectifier will supply direct current more economically for telephone calls. It can also be adapted to important uses in television, computers, industrial machines, and military equipment. Thus, Bell Telephone Laboratories research continues to improve telephony—while it helps other fields vital to the nation.



Above, new rectifier (held in pliers) is contrasted with comparable tube rectifier and its filament transformer, rear. Mounted on a cooling plate, lower center, the new rectifier can easily supply 10 amperes of direct current at 100 volts, that is 1000 watts—enough to power 350 telephones.

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Editorial

Flood Control

ANYONE WHO PREFERS rich green grass to starved yellow grass, trees with birds instead of beetles, brooks full of trout rather than just muddy water will enjoy reading Louis Bromfield's books "Pleasant Valley," "Malabar Farm," and "Out of the Earth." Mr. Bromfield rescued a thousand acres of "worn out" Ohio farm land and converted them into a thriving dairy farm; Malabar Farm has become a national showplace.

One of the first problems was local flood control. The eroded, gravelly hillsides were dug up, filled with organic trash, and planted with deep-rooted legumes and grasses. The hard-silted bottom fields were broken up deeply so that water could penetrate the hardpan layer formed by years of shallow cultivation. A couple of ponds were constructed and a brook dammed. Now the rainwater runoff is small, the streams no longer race over their banks each spring, muddy with topsoil, nor do they dry up to dirty puddles each summer.

Mr. Bromfield has an emphatic message about soil conservation and flood control. The permanent solution to floods along the Mississippi is not longer and higher levees near New Orleans, nor is it huge, expensive dams halfway up the river and its big tributaries. Rather, thousands of small ponds and lakes are needed, impounding the waters of the smallest brooks in the watershed. And the adjacent lands should be so managed as to retain as much rainfall as possible.

Fifty years ago a disastrous flood raced down the Miami River valley of Ohio. Dayton and other cities were hard hit; smaller communities and lone farmers were simply swept away. After ten years of wrangling, a control and conservancy plan was adopted. Now the valley is dotted with small lakes and ponds (in places even beavers were introduced to assist), and large and small earth dams were constructed to create "dry reservoirs" ready to impound flood waters if need be. Farmers may cultivate the fields inside these reservoirs at their own risk; they have suffered little loss. On several occasions rainfall and flood potential have been as great as at the time of the original disaster, but very little damage resulted.

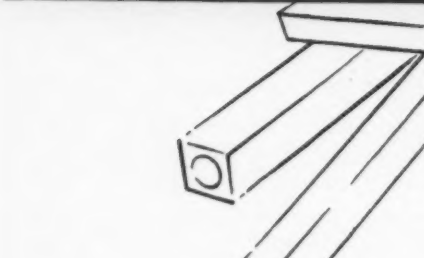
Northeastern states suffered $1,600,000,000 damage in the unprecedented torrential rains of August 1955. Several hundred people lost their lives, thousands their homes, and even more lost their jobs. The local "flash floods" alone would have done much damage, but when followed by walls of water racing down whole valleys the result was disaster.

Parts of New England had warning of what damage a hurricane-flood can do in 1938. One result was the construction of an $11,000,000 flood wall at Hartford, Conn. This wall is credited with saving up to $20,000,000 in damage in 1955. The Army Corps of Engineers has recommended a $300,000,000 flood control program in New England, of which only one-sixth has been carried out. Lt. General Samuel D. Sturgis, Chief of the Corps, estimates that if the full program had been completed, the major part of the 1955 damage would have been prevented. Now he advises that the program be re-examined and perhaps considerably broadened, since it seems possible that the path of Atlantic hurricanes is changing.

A major difficulty is naturally a wrangle among the various states involved. The up-river states dislike to provide land for dams and reservoirs even if the Federal Government provides funds. These states should study the Ohio plan. The controlled valleys have a greater agricultural potential than before, there is hunting and fishing unexcelled in most of the nation, there are camping and vacation resorts. Many an industrial worker can drive a few miles with his family to a lake shore picnic spot for a day, or even for a little recreation after work. The upkeep is paid for by licences and rentals. The up-stream population has not suffered in helping to protect its down-stream neighbors.

—CVK

Photo shows a battery of Hooker type S-3A cells as used by licensees of Hooker Electrochemical Company.



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Current Affairs

News Notes in the Electrochemical Field

1954 Semiconductor Abstracts Available

"Abstracts of the Literature on Semiconducting and Luminescent Materials and Their Applications—1954 Issue" will be available about November 15. With the 1954 issue, two full years of organized abstracts on the solid state electronic device industry can be obtained from John Wiley & Sons, Inc. 440 Fourth Avenue, New York, N. Y. The 1954 Issue, like the 1953, was compiled by Battelle Memorial Institute and sponsored by The Electrochemical Society.

The 1954 format is essentially the same as the 1953 issue, providing even greater detail in each abstract. Over 220 abstracted articles are devoted to germanium, silicon, and their applications. The entire volume contains abstracts of over 750 articles.

To persons concerned with the broad, growing field of semiconducting and luminescent materials and their applications, keeping up with the contributions from so many branches of science is an almost hopeless task since articles appear in so many different periodicals published all over the world. To service these and other interested people, The Electrochemical Society initiated a long-range project last year to publish annually abstracts, prepared by Battelle Memorial Institute, in this field.

Members of the Society who wish to buy the book, listed at $5.00, at the 33⅓% member discount should send their orders to The Electrochemical Society, 216 West 102nd St., New York 25, N. Y. The Society will then forward orders to John Wiley & Sons, Inc., who will ship the volume with the invoice. To receive the member discount, *orders must* be sent to Society Headquarters.

Expanded Rare Earths and Thorium Program

W. R. Grace & Co. recently announced that its Davison Chemical Co. Division and Rare Earths, Inc., Pompton Plains, N. J., a wholly owned subsidiary, have joined in a program of expanded production, sales, research, and development of rare earths and thorium.

Rare Earths, Inc., has a plant in operation at Pompton Plains for processing rare earths and thorium from monazite sands, and additional facilities are being installed at Davison's Curtis Bay Works, Baltimore.

To coordinate Grace's interests in the field of industrial atomic energy, Davison has formed an Atomic Developments Dept. with headquarters at Baltimore. Dr. Allen T. Cole, formerly manager of the company's Florida Phosphate Division, has been named as manager.

Industrial Research Center

Appropriately in this year of 1955, which marks the 75 birthday of the University of Southern California and the golden anniversary of its first engineering courses, plans are under way for the establishment on campus of a $1,000,000 Southern California Industrial Research Center.

Ground will be broken late this fall for the first of four building units which will comprise an extension to the present School of Engineering building. Three of the initial units are designed to accommodate mechanical and aeronautical engineering, electronics and electrical engineering, chemical and petroleum engineering. The fourth will serve as a headquarters unit. In the future, additional classrooms, a library, and an alumni wing will be constructed.

I.E.S. 47th Annual Conference

The latest advances in lighting research and application were presented at the National Technical Conference of the Illuminating Engineering Society, September 12–15, at the Statler Hotel in Cleveland. The registration of members and guests totaled 1000.

In addition to general and application sessions and the opening session, complete technical sessions were devoted to: Light Sources, Residential Lighting, Lighting Calculations, Research, Architectural Lighting, Daylighting, Street Lighting.

The program included some 35 technical papers as well as a review of the year's achievements in the art of illuminating engineering. Also included was a Lighting Service Forum under the Chairmanship of Lee E. Tayler devoted to the national competition of 10 regional winners in the Most Interesting Lighting Job Contest.

Duncan M. Jones of Curtis Lighting, Ltd., Montreal, and President of the Illuminating Engineering Society, addressed the opening session of the Conference and presented R. F. Hartenstein, Ohio Edison Co., Akron, incoming administration President, to the delegates at the Conference banquet.

The Society's Gold Medal was presented at the opening session to J. L. Stair, for many years associated with Curtis Lighting Co. of Chicago.

Plenary World Power Conference

United States engineers, scientists, industrialists, and government representatives will present 25 papers on the development of atomic energy, steam and gas turbines, and related subjects of power and fuel technology at the fifth plenary meeting of the World Power Conference in Vienna, June 17–23, 1956, it was recently announced by Gail Hathaway, Chairman of the United States National Committee.

Most of the 45 member nations are expected to participate. The general theme will be "World Energy Resources in the Light of Recent Technical and Economic Developments." The U. S. Government is expected to be represented. The Atomic Energy Commission, Bureau of Mines, Bureau of Reclamation, Corps of Engineers, Federal Power Commission, and Rural Electrification Administration are members of the U. S. National Committee and representatives of several of these agencies will present papers.

Improved G-E Mercury Lamps

The General Electric Co. recently announced improvements to four of its 400-watt mercury lamps. The lamps now produce from 5 to 12 per cent more light initially, give better light main-

tenance, have longer life, and are more uniform. The improvements are the latest in a series which have been made since early 1954.

In the new construction of the lamps, silver-plated wire replaces metal bands in the framework of the mount, which supports the mercury element inside the outer bulb. The silver finish reflects light which heretofore has been absorbed by the dull metal bands, and the wire framework permits more light to get out than did the old bulkier construction.

Other production techniques employed to increase light output include a new method of making electrodes which virtually eliminates impurities and reduces tube darkening, extremely accurate measurement of mercury for each arc-tube, the relocation of the resister so that it cannot absorb light, and the washing of quartz parts in a series of cleansing acid baths to remove impurities which could reduce light output or shorten life.

Help Wanted on New Handbook

Your hobby, preoccupation, or annoyance with terminology and nomenclature problems can help an important project in the field of military engineering. If there is a chance that your subject field might be of interest in ordnance work, and if you have either formal or informal collections of terminologies, glossaries, specialized dictionaries, or references to them, please contact: Allen Kent, Associate Director, Center for Documentation and Communication Research, School of Library Science, Western Reserve University, Cleveland 6, Ohio.

Several months ago, the Army Ordnance Corps initiated the preparation of a comprehensive Ordnance Engineering Design Handbook to summarize fundamental principles and basic design data. The handbook is being written to provide needed information to army ordnance and arsenal personnel and to the engineering staffs of contractors having ordnance design responsibilities. It will consist of approximately 180 sections of about 100 pages each. Completion of the first edition is expected to require about five years.

Over-all editorial responsibility for the Handbook has been assigned to the Ordnance Engineering Handbook Office established by the Office of Ordnance Research at Duke University, Durham, N. C. The Center for Documentation and Communication Research at Western Reserve University, Cleveland, is cooperating with the Engineering Handbook Office in the important area of terminology definition.

Pennsalt District Sales Territory

Cincinnati has been selected as headquarters of a new district sales territory for the Metal Processing Chemicals Dept. of the Pennsylvania Salt Manufacturing Co.

Directed by district sales manager Bill Wilson, the staff will include sales representatives Jack Cram, Frank Wilcher, and Clay Brahm, and technical services representative Allan Lenio.

Journal of Electronics

Publication of Vol. I, No. 1, of a new periodical, *Journal of Electronics*, has been announced by Academic Press Inc., distributors of the journal in the United States and Canada. This new journal will serve as a forum for electron physicists, solid state physicists, chemists, and engineers, and will contain accounts of both theoretical and experimental work.

Dr. J. Thomson of the Royal Naval Scientific Service will act as Editor, and Professor N. F. Mott, F. R. S., will be the Consultant Editor.

Vol. I, of about 600 pages, which will be released in six parts, is priced at $15.40; single issues are available at $2.80. Orders originating in the United States and Canada should be addressed to Academic Press Inc., 125 East 23 St., New York 10, N. Y.

General Instrument—Automatic Enters Semiconductor Field

Silicon power rectifiers which are stated to be "the smallest, lightest, and most efficient ever marketed" (taking up only $^{3}/_{100}$ of a cubic inch of space and weighing $^{7}/_{100}$ of an ounce) have been developed by the Automatic Manufacturing Corp., subsidiary of the General Instrument Corp. The rectifiers, now in production at the company's Newark plant, are the first products to emerge from the recently established Semi-Conductor Department which will develop and mass produce semiconductor devices for industry and the military.

Automatic Manufacturing and its parent, General Instrument Corp., are leading producers of radio, TV, and electronic components for industrial, commercial, and military uses. The company's program in the semiconductor field calls for the use of manufacturing processes which will produce the new devices "at commercially feasible prices and with uniform reliability" through mechanization and automation.

Smith Memorial Collection Reopened

The University of Pennsylvania has announced that its Edgar Fahs Smith Memorial Collection in the History of Chemistry has been reopened for service in new quarters on the university campus. It is now located in Rm. 420 of the Hare Bldg., 36th and Spruce Sts., Philadelphia.

The Smith Collection was presented to the university in 1928 after the death of Dr. Edgar Fahs Smith, who had been provost and professor of chemistry. Until last fall it was housed in Dr. Smith's old office in the Harrison Laboratory of Chemistry. With the collection's growth, its quarters became inadequate. Originally consisting of some 7000 items, it had grown to include more than 9000 books and pamphlets, nearly 1400 manuscripts, 3400 portrait prints and medals of chemists, and various items of chemical apparatus. It had become the largest public collection in its field in the United States.

Dr. Claude K. Deischer, assistant director of the Harrison Laboratory, has been appointed acting curator of the Smith Collection. In addition, Mrs. Elisabeth H. Hansell has been named custodian and is on duty from 9:30 A.M. to 12:30 P.M. daily except Saturdays and Sundays. Requests for service may be addressed to Mrs. Hansell.

Becco Expands Hydrogen Peroxide Facilities

Multimillion dollar plant expansion programs involving the hydrogen peroxide producing facilities at Buffalo, N. Y., and Vancouver, Wash., of the Becco Chemical Division, Food Machinery and Chemical Corporation, were announced recently by Dr. M. E. Bretschger, Divisional President.

Becco's Vancouver plant, which is said to be the world's most modern and efficient facility for the electrolytic production of hydrogen peroxide, will be enlarged by approximately 50%. The estimated cost for the Vancouver expansion is more than one million dollars. Contracts have been signed for the construction of the necessary buildings and the installation of the equipment. Production is anticipated in the early part of 1956.

Buffalo Electro-Chemical Company,

Inc., predecessor to the Becco Chemical Division, has long been a leader in the field of hydrogen peroxide production. This company was the first to introduce the electrolytic process in the United States. Today, Becco operates in its Buffalo and Vancouver plants the country's largest total capacity employing this procedure.

G. E. Metals and Ceramics Processing Lab.

A research facility to provide new materials for the future was recently dedicated at the General Electric Research Laboratory, Schenectady, N. Y. The principal speaker at the ceremonies was Donald A. Quarles, newly nominated by President Eisenhower to serve as Secretary of the Air Force.

Dedication on August 26 of the new $5 million Metals and Ceramics Building concluded a week-long program of conferences and seminars attended by some of the nation's leading scientists, professors of metallurgy and ceramics, and representatives of the G. E. operating components to be served by the new laboratory facility.

Completion of the Metals and Ceramics Building is part of a $13 million expansion program for the Research Laboratory at The Knolls.

Bright Nickel Plating

The S. E. & M. Vernon Co.'s conversion to the bright nickel plating process (a development of the Hanson-Van Winkle-Munning Co., Matawan, N. J.) has resulted in 20% faster plating and savings of 50% in amperage and 25% in nickel. In addition, the process has cut purification, heat, power operating, and maintenance costs because of its higher stability and lower operating temperature.

The company, located in Elizabeth, N. J., is one of the nation's largest manufacturers of looseleaf binders and folders.

Low-Expansion Cobalt-Iron-Chromium Alloys

The National Bureau of Standards has confirmed that the thermal expansion of certain cobalt-iron-chromium alloys is extremely low and nearly constant between 20° and 60°C. This information has resulted from thermal expansion and phase transformation studies on a number of these alloys by Peter Hidnert and Richard K. Kirby of the Bureau staff.

The Bureau's investigation indicates the existence of an alloy (36.6% iron, 8.9% chromium, and the balance cobalt) with a coefficient of expansion less than 1×10^{-6}/°C for the range from 20° to 60°C. However, it was found that the low expansion of such alloys is very sensitive to small variations in their chemical composition. In addition, some of them undergo a transformation on cooling at low temperatures.

Further research is necessary to develop additional information on the physical properties of these low-expanding alloys at various temperatures.

Faraday Disc. No. 5 Wanted

Will anyone who has a copy he no longer needs of the *Discussions of The Faraday Society*, No. 5, entitled "Crystal Growth," please contact: Mrs. J. M. Fertig, Research Library, Westinghouse Research Labs., Beulah Rd., Churchill Borough, Pittsburgh 35, Pa.

DIVISION NEWS

Electronics Division

Semiconductor Symposium, May 1956

The fourth annual Semiconductor Symposium of The Electrochemical Society will be held on April 29, 30, and May 1, 2, and 3, 1956 at the Mark Hopkins Hotel in San Francisco, Calif. This notice is an invitation to submit papers for presentation. Early plans are to divide the sessions as follows:

(*A*) Two half-day sessions on semiconducting materials—elemental, alloys, and compounds.

(*B*) A half-day session on surface controlled phenomena.

(*C*) A half-day session on chemical process technology.

In each of the areas of interest we would like to present a balanced agenda including one review paper of the state of each field, 30-minute presentations (including discussion time) of new information which can be scheduled by midwinter 1955, and a number of shorter presentations of about 10 minutes' duration of the, "late news" type.

If you wish to present papers, will you please notify the undersigned as follows:

(*A*) Signify interest in participating and title of proposed paper as early as possible, no later than November 15, 1955. Such information is needed for agenda planning purposes.

(*B*) Submit an abstract of approximately 75 words no later than January 2, 1956. This abstract will be printed in the general program for the meeting.

(*C*) Submit a second "extended abstract" of about 1000 words along with brief pertinent data, illustrations, curves, etc., not later than February 1, 1956. This extended abstract is "printed, but not published" in a booklet "Enlarged Abstracts of Papers Presented by the Electronics Division" and is available at the meeting at cost.

Plans for the ten-minute "late news" type of papers are as follows:

(*A*) Notify the General Chairman (writer of this notice) as soon as it appears likely that you will be able to present a "late news" paper, giving title or general area of interest.

(*B*) Submit 75-word abstracts no later than April 8, 1956. These titles and abstracts will not be in the Meeting Program or the Enlarged Abstracts, but arrangements will be made to have mimeographed copies available prior to the meeting.

J. W. Faust, Jr.
(*1956 Chairman Semiconductor Symposium*)
Mailing Address:
Westinghouse Research Laboratorise
Beulah Road, Churchill Borough
Pittsburgh 35, Pa.

Notice to Members

By now you have received your official voting ballot from Society Headquarters. If you have not already done so, please return the ballot by *December 15* so that your vote may be included in the final election count.

E & M Rare Earth Symposium, May 1956

The Electrothermics and Metallurgy Division is soliciting papers for the April 29–May 3, 1956 Society Meeting in San Francisco. The subject of one symposium will be "Rare Earths." Original papers are requested rather than reviews of previously reported studies. Also, a number of papers in the general field of chemical metallurgy are desired.

Authors who wish to present papers should submit a *75-word abstract* to W. H. Smith, General Electric Research Laboratory, P. O. Box 1088,

Schenectady, N. Y., *not later than January 2, 1956.*

SECTION NEWS

Midland Section

The officers of the Midland Section for the coming year are:

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Vice-Chairman—P. R. Juckniess, 1408 Crane Court, Midland, Mich.

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H. A. Robinson, 616 E. Grove St., Midland, Mich.

PAUL R. JUCKNIESS,
Vice-Chairman

NEW MEMBERS

In September 1955 the following were approved for membership in The Electrochemical Society by the Admissions Committee:

Active Members

HOWARD F. BARTRAM, Great Northern Carbon and Chemical Co., Ltd., Rm. 625, Dominion Square Bldg., Montreal, Canada (Corrosion, Electrothermics & Metallurgy, Industrial Electrolytic)

ERIK BLOMGREN, The Chemical Institute, University of Uppsala; Mail add: Lästmakargatan 12 B, Uppsala, Sweden (Battery, Corrosion, Electronics, Theoretical Electrochemistry)

MARY JO BOEHM, Naval Research Lab., Code 6380, Washington 25, D. C. (Corrosion)

RAYMOND G. CHELTON, Armour Research Foundation, 10 W. 35 St., Chicago 16, Ill. (Corrosion)

JOHN B. EISEN, Bjorksten Research Labs., Inc.; Mail add: Box 27, Waterloo, Wi (Theoretical Electrochemistry)

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MAX M. GRANSDEN, Canadian Marconi Co.; Mail add: 52 Charles Ave., Valois, Montreal 33, Que., Canada (Electronics)

CHARLES J. GUARE, General Electric Co., Building #37, Rm. 254, Schenectady, N. Y. (Corrosion)

DONALD J. HANSEN, Metals Research Labs., Electro Metallurgical Co.; Mail add: 4896 University Court, Niagara Falls, N. Y. (Industrial Electrolytic, Theoretical Electrochemistry)

IMRE J. HEGYI, RCA Labs., Princeton, N. J. (Electronics)

JAMES C. HICKLE, General Electric Co.; Mail add: 316 E. Ninth St., Owensboro, Ky. (Electronics)

WILLIAM H. KIMBERLY, Douglas Aircraft Co., 827 Lapham St., El Segundo, Calif. (Corrosion)

LOUIS H. LA FORGE, JR., Stanford University, W. W. Hansen Labs. of Physics; Mail add: 764 Marion Ave., Palo Alto, Calif. (Electric Insulation, Electrodeposition, Electronics)

FRANK MATOSSI, Naval Ordnance Lab.; Mail add: 1215 Simmons Dr., Rockville, Md. (Electronics)

QUENTIN H. MCKENNA, Horizons Inc.; Mail add: 5533 Biddulph Ave., Cleveland 9, Ohio (Industrial Electrolytic)

RICHARD J. MILLARD, Sprague Electric Co., North Adams, Mass. (Electric Insulation)

SOL NUDELMAN, Naval Ordnance Lab., White Oak, Md. (Electronics)

CHARLES J. OWEN, United States Steel; Mail add: 822 N. St. Clair St., Pittsburgh 6, Pa. (Electrodeposition)

JOHN W. PAULSON, Ray-O-Vac Co.; Mail add: 106 Craig Ave., Madison 5, Wis. (Battery)

STEPHEN PISHKO, Electro Metallurgical Co.; Mail Add: 357 Fourth St.,

ECS Membership Statistics

The following two tables give breakdown of membership as of October 1, 1955. 73 delinquents were removed from the rolls as of May 1, 1955. The Secretary's Office feels that a regular accounting of membership will be very stimulating to membership committee activities. In Table I it should be noted that the totals appearing in the right-hand column are *not* the sums of the figures in that line since members belong to more than one Division and, also, because Sustaining Members are not assigned to Divisions. But the totals listed are the total membership in each Section. In Table I, Sustaining Members have been credited to the various Sections.

TABLE I. *ECS Membership by Sections and Divisions*

Section	Division												
	Battery	Corrosion	Electric Insulation	Electrodeposition	Electronics	Electro-Organic	Electrothermics & Met.	Industrial Electrolytics	Theoretical Electrochem.	No. Division	Totals as of 10/1/55	Totals as of 1/1/55	Net Change
Chicago	11	30	4	46	13	9	10	13	17	15	105	102	+3
Cleveland	43	37	4	46	33	10	20	28	43	18	173	150	+23
Detroit	5	16	6	34	6	8	4	3	20	20	74	67	+7
India	6	1	1	9	2	4	2	9	7	3	22	23	−1
Midland	5	12	0	3	1	2	6	15	7	4	37	36	+1
New York	62	97	19	127	64	25	45	53	73	72	414	374	+40
Niagara Falls	6	19	0	16	2	6	52	46	13	26	139	105	+34
Pacific Northwest	5	11	0	8	1	2	4	13	13	5	38	29	+9
Philadelphia	20	27	4	39	42	17	18	14	45	29	163	144	+19
Pittsburgh	3	28	3	21	9	5	19	14	26	12	80	69	+11
San Francisco	6	10	1	11	7	3	7	17	10	3	41	38	+3
Washington-Baltimore	33	36	9	33	17	3	11	13	29	7	110	104	+6
Quebec-Ontario	7	11	0	13	0	3	22	20	5	13	58	43	+15
U.S. Non-Section	67	147	29	158	85	49	95	94	140	102	627	581	+6
Foreign Non-Section	29	39	6	44	16	23	25	48	50	57	170	176	+6
Total as of Oct. 1, 1955	308	521	86	608	298	169	340	400	498	386	2251		
Total as of Jan. 1, 1955	281	516	81	590	276	169	309	374	460	306		2141	
Net Change	+27	+5	+5	+18	+22	0	+31	+26	+38	+80			

TABLE II. *ECS Membership by Grade*

	Total as of 10/1/55	Total as of 1/1/55	Net Change
Active	2006	1889	+117
Life	14	14	0
Emeritus	35	39	−4
Associate	50	63	−13
Student	41	31	+10
Honorary	5	5	0
Sustaining	100	100	0
Total	2251	2141	+110

Lewiston, N. Y. (Electrothermics & Metallurgy)

C. A. ROBAK, Norsk Akkumulator Co. A/S, Horten, Norway (Battery)

RAYMOND C. SANGSTER, Texas Instruments Inc.; Mail add: 3312 Hedgerow Dr., Dallas, Texas (Electronics)

GEORGE P. SMITH, JR., Oak Ridge National Lab., Oak Ridge, Tenn. (Theoretical Electrochemistry)

WILLIAM H. SMITH, General Electric Research Lab., P. O. Box 1088, Schenectady, N. Y. (Electrothermics & Metallurgy)

JOHN C. TRACKMAN, Brown Boveri Corp.; Mail add: 12 S. Brookwood Dr., Montclair, N. J. (Electronics, Industrial Electrolytic)

LILY WEIDENFELD, The Polytechnic Institute of Brooklyn, 85 Livingston St., Brooklyn 1, N. Y. (Electronics)

GUNTHER A. WOLFF, Signal Corps Engineering Labs., Components Div., Chemical Physics Branch, Ft. Monmouth, N. J. (Electronics)

Student Associate Members

SHELDON EVANS, New York University; Mail add: 143-35 Hoover Ave., Jamaica, N. Y. (Corrosion, Theoretical Electrochemistry)

FRANK J. MARASA, Radio Receptor Co.; Mail add: 34-22 Astoria Blvd., Long Island City 3, N. Y. (Electronics)

ROBERT M. SKOMOROSKI, New York University, Chemistry Dept., Washington Square, New York 3, N. Y. (Corrosion)

Transfer from Student Associate to Active Membership

WATT W. WEBB, Metals Research Labs., Union Carbide and Carbon Corp., P. O. Box 580, Niagara Falls, N. Y. (Theoretical Electrochemistry)

Reinstatements to Active Membership

HOLBERT E. DUNN, Vanadium Corp. of America; Mail add: 80 N. Emily St., Pittsburgh 5, Pa. (Electrothermics & Metallurgy)

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B. K. RAM PRASAD, Government of Bombay and The Bombay Electricity Board, Mercantile Bank Bldg., Bombay 1, India (Battery, Electric Insulation, Electrodeposition, Electro-Organic, Electrothermics & Metallurgy, Industrial Electrolytic, Theoretical Electrochemistry)

Reinstatement and Transfer from Student Associate to Active Membership

LAWRENCE R. SCHARFSTEIN, Westinghouse Electric Corp.; Mail add: 5453 Youngridge Dr., Pittsburgh 36, Pa. (Corrosion, Theoretical Electrochemistry)

Deceased Members

RAY H. WHITE, Summerville, S. C.
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G. A. ROUSH, Arlington, Va.

PERSONALS

ANDREW DRAVNIEKS has been appointed Head of the Corrosion Section in the Materials Division, Engineering Research Dept., Standard Oil Co. (Indiana), Whiting, Ind.

ALBERT H. COOPER, professor of chemical engineering at the University of Maryland, has been named Chairman of the Dept. of Chemical Engineering at Pratt Institute, Brooklyn, N. Y. Dr. Cooper is also Manager of the Pilot Engineering Co. and Vice-President and Technical Director of the Chemchron Corp.

CLIFFORD A. HAMPEL

CLIFFORD A. HAMPEL has joined the Fansteel Metallurgical Corp., North Chicago, Ill., as Manager of the Chemical Equipment Division, to be responsible for engineering, design, and sales of products to the chemical process industries, including acidproof tantalum equipment. The division will be concerned with applications of the refractory metals, tantalum, columbium, molybdenum, tungsten, and their derivatives in the chemical process industries.

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RALPH J. BRODD recently completed study for the Ph.D. degree at the University of Texas. He is now employed in the Electrochemistry Section of the Electricity and Electronics Division at the National Bureau of Standards, Washington, D. C., where his field of research will be in reactions at electrode surfaces.

MEETINGS OF OTHER ORGANIZATIONS

NACE Western Region Meeting, Sir Francis Drake Hotel, San Francisco, Calif., Nov. 17–18.

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS, Annual Meeting, Statler Hotel, Detroit, Mich., Nov. 27–30. Further information from: Stephen L. Tyler, Executive Secretary, 25 W. 45th St., New York 36, N. Y.

AMERICAN INSTITUTE OF ELECTRICAL ENGINEERS (AIEE), Committee on Technical Operations, 1956 Winter Meeting, General, Hotel Statler, New York, N. Y., Jan. 30–Feb. 3, 1956.

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS, Los Angeles, Calif., Feb. 26–29, 1956.

AMERICAN SOCIETY FOR TESTING MATERIALS, 1956 Committee Week, Hotel Statler, Buffalo, N. Y., Feb. 27–March 2, 1956.

AIEE, National Meeting, Bradford Hotel, Boston, Mass., April 26 and 27, 1956.

ASTM, 1956 Annual Meeting, Chalfonte-Haddon Hall Hotel, Atlantic City, N. J., June 17–22, 1956.

1956 BOUND VOLUMES

Members and subscribers who wish to receive bound copies of Vol. 103 (for 1956) can receive the volume for the low, prepublication price of $6.00 if their orders are received at Society Headquarters, 216 West 102nd St., New York 25, N. Y., by *December 1*. After that date members will be charged $12.00 and nonmembers, including subscribers, $18.00.

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ANNOUNCEMENTS FROM PUBLISHERS

ANNOTATED BIBLIOGRAPHY ON THE USE OF ORGANOLITHIUM COMPOUNDS IN ORGANIC SYNTHESIS, Supplement No. 3. Published by the Lithium Corporation of America, Inc., 2526 Rand Tower, Minneapolis 2, Minn. Distributed without charge to those engaged in chemical research, the Original Bibliography and its Supplements (1, 2, and 3) are offered as a reference work and guide to research on lithium and its compounds.

PRODUCTION CONTROL THROUGH ELECTRONIC DATA PROCESSING: A CASE STUDY. Order PB 111580 from Office of Technical Services, U. S. Dept. of Commerce, Washington 25, D. C. 52 pages, $1.50.

Report prepared under Office of Naval Research contract is a case study of production control through electronic data processing, written by an electronic data systems engineer to give business management a better picture of the use of electronic systems.

HIGH TEMPERATURE DATA. Published by the National Association of Corrosion Engineers, 1061 M & M Bldg., Houston, Texas. 50 cents. Report, compiled by Technical Unit Committee T-5B on High Temperature Corrosion, contains information on the high temperature corrosion behavior of 31 materials ranging from cast iron to lead and including some nonmetallics.

Volumes Wanted

Will anyone who has a copy he no longer needs of Vol. 86 (1944) and 92 (1947) of the TRANSACTIONS please contact Toshio Keta, 4307 Sheridan St., University Park, Hyattsville, Md.

EMPLOYMENT SITUATIONS

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CHEMIST, 36, 11 years' experience, including batteries, electroplating, general physical and chemical commerical testing, seeks New Jersey, Philadelphia, New York City position. *Reply to Box 357.*

CHEMICAL ENGINEER, 40, B.S. degree, 14 years' experience, including materials engineering and research, electrodeposition processes, product engineering and development work involving capacitors. *Reply to Box 358.*

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ENGINEER, development, for work in rapidly expanding and progressive battery company. Previous work in battery, electroplating, or electrical component manufacture desirable but not essential. Must be alert, dextrous, and have a working knowledge of laboratory techniques. Must be U. S. citizen. State salary desired. Submit resume to Yardney Laboratories, 40 Leonard St., New York 13, N. Y.

ENGINEERS, ELECTRONIC SCIENTISTS, METALLURGISTS, PHYSICISTS, PHYSIOLOGISTS, PSYCHOLOGISTS, TECHNOLOGISTS. The Naval Air Material Center, located at the Naval Base, Philadelphia, Pa., has vacancies in the above engineering and scientific positions which must be filled. The Center is engaged in an extensive program of aeronautical research, development, experimentation, and test operations for the advancement of Naval Aviation. Engineering vacancies exist in the following options: Electrical, Electronics, General, Industrial, Mechanical, Structural, and Aeronautical (various suboptions). Starting salaries range from $3670 to $8990 per annum. Application for Federal Employment, Standard Form 57, should be filed with the Industrial Relations Dept., Naval Air Material Center, Naval Base, Philadelphia 12, Pa. Applications may be obtained from the above address or information as to where they are available may be obtained from any first or second class post office.

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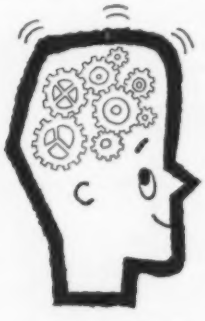

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The Electrochemical Behavior, Including Hydrogen Overvoltage, of Iron in Acid Environments[1]

MILTON STERN[2]

Corrosion Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts

ABSTRACT

The corrosion rate of pure iron in deaerated acid media was studied as a function of *p*H. The rate was found to be essentially independent of *p*H over the range 1–4 in 4% sodium chloride. Potential and polarization measurements are used to explain this behavior. A method for calculation of corrosion rates from electrochemical measurements alone is described. Limitations and environmental conditions required for this method are discussed.

INTRODUCTION

The purpose of this investigation is to show the relations that exist between the electrochemical behavior of pure iron and its corrosion rate in oxygen-free, acid environments. Such information permits a better understanding of the fundamental factors which influence the corrosion rate and supplies a basis for predicting corrosion rates of iron and steel from independent data. Additional information concerning the effect of various alloy additions will be published later.

Recently, D'Ans and Breckheimer (1) reported potential measurements for carbonyl and electrolytic iron in a variety of air-free, acid media as a function of *p*H. They found for each system examined that a *p*H range exists within which the corrosion potential varies by approximately 0.059 volt for each unit *p*H change. The range over which this behavior holds varies, depending on the electrolyte and ferrous ion concentrations, but in general falls within *p*H values 1–5. Similar results have been reported by Bonhoeffer and Jena (2) and by Bodforss (3).

This means that over a given *p*H range, the steady-state corrosion potential of an iron electrode appears to behave in much the same manner as a reversible hydrogen electrode ($dE/dp\mathrm{H} = 0.059$), with absolute value of the iron potential being more active than a hydrogen electrode in the same solution. A general summary of data up to 1938 is provided by Gatty and Spooner (4), and an explanation of the effect of *p*H is suggested by Uhlig (5) who showed, in accord with the electrochemical theory of corrosion, that the observed iron potential is a result of surface anode and cathode potentials polarized by local action currents.

[1] Manuscript received March 17, 1955. This paper was prepared for delivery at the Boston Meeting, October 3 to 7, 1954.

[2] Present address: Metals Research Laboratories, Electro Metallurgical Company, Niagara Falls, New York.

Since it is known that the potential of iron is determined by local polarization characteristics, an explanation of the above potential behavior resides in a determination of hydrogen overvoltage, anodic polarization, and corrosion rate.

APPARATUS AND PROCEDURES

It was desirable to determine the relations between corrosion rate, corrosion potential, hydrogen overvoltage, and anodic polarization; therefore, arrangements were made to measure all these properties in the same equipment under the same conditions. This was achieved in the cell illustrated in Fig. 1, holding about 2 liters of electrolyte.

Deaeration was accomplished by passing purified electrolytic hydrogen through the solution for a minimum of 6 hr. The gas was purified by passing over copper chips at 500°C, ruthenium catalyst at 300°C, and finally over palladium catalyst at room temperature. With momentary increase of hydrogen flow rate, the specimen was introduced into the cell, and deaeration continued for about 4 hr. The hydrogen was then by-passed over the top of the solution by turning appropriate stopcocks and a slight positive pressure maintained in the vessel. All tests were conducted in unstirred solutions except where otherwise indicated.

The amount of corroded iron was determined by periodically withdrawing and analyzing known quantities of solution, using the orthophenanthroline colorimetric method (6). Analyses were continued until a steady state was reached. The minimum test time was 75 hr, with the majority of measurements being taken over periods averaging 150 hr. Reported corrosion rates were determined from the slope of the linear portion of weight loss-time curves.

Corrosion potentials were measured using a platinized platinum reference electrode immersed directly in the same solution. This hydrogen electrode

was compared before and after each run with a glass electrode using a Beckman Model G meter.

After steady state was achieved, indicated by a constant corrosion potential and corrosion rate, two auxiliary iron electrodes were immersed in the solution along with a salt bridge probe which could be brought up to the surface of the corroding specimen by rotating two eccentric joints at the top of the cell. The salt bridge was filled with solution taken from the corrosion cell. Cathodic polarization measurements were conducted prior to similar anodic measurements. It was found that cathodic polarization did not affect appreciably the corrosion potential of an electrode after the applied current was stopped. Anodic measurements, however, caused a pronounced shift of corrosion potential in a manner which will be discussed later, and several hours were necessary thereafter for the sample to return to its original steady state.

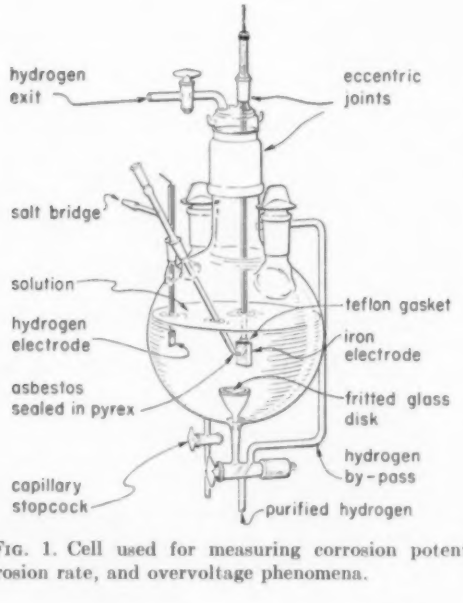

FIG. 1. Cell used for measuring corrosion potential, corrosion rate, and overvoltage phenomena.

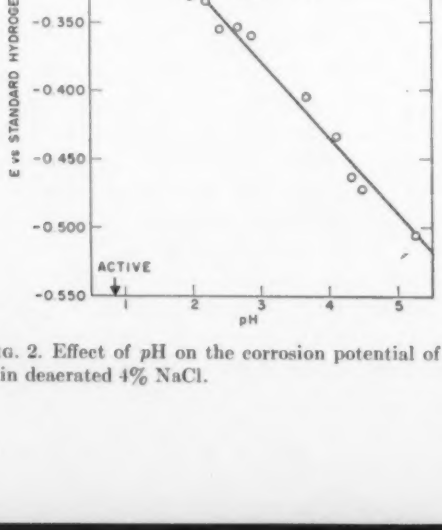

FIG. 2. Effect of *p*H on the corrosion potential of pure iron in deaerated 4% NaCl.

During prolonged polarization, when chemical changes became greater, it was necessary to separate anodic and cathodic compartments. Therefore, the cell of Fig. 1 was modified into a three-compartment cell separated by fine glass fritted disks. The outer compartments, each approximately 200 ml in volume, and containing iron auxiliary electrodes, could be deaerated in the same manner as the larger center compartment.

Electrodes were cut from research-grade, high-purity iron originally made from carbonyl iron which was melted, purified, and cast under high vacuum. The analysis received from the supplier[3] was 0.005% carbon, 0.023% oxygen, and 0.0002% nitrogen. No further analysis was obtained, but presumably the other impurities present were within the limits claimed by the supplier who indicated the iron content as 99.95–99.98%. Surfaces were filed and abraded smooth, pickled a number of times in concentrated nitric acid followed by concentrated hydrochloric acid to remove the cold-worked surface, rinsed thoroughly in distilled water, and immediately placed in the solution. It was found that this procedure allowed steady-state attainment in a minimum time. Electrical contact was achieved by silver soldering a $\frac{1}{16}$-in. drill rod to a stem machined on the electrode, the drill rod and stem being isolated from the solution by a glass tube and a thick Teflon gasket (Fig. 1).

Solutions were prepared from distilled water and reagent-grade chemicals. The *p*H of sodium chloride solution was adjusted with hydrochloric acid. The latter solutions were pre-electrolyzed between platinum electrodes at a current density of 15 μa/cm^2 for 24 hr. All measurements were conducted in a thermostated room maintained at 25°C ± 1°C.

RESULTS

Corrosion potential.—The variation of corrosion potential of pure iron in 4% sodium chloride as a function of *p*H is presented in Fig. 2. It is important to note that the variation of potential with *p*H is close to, but below, the value for a reversible hydrogen electrode. The slope $dE/dp\text{H} = 0.0559$ was determined by the method of least squares. Fig. 2 also illustrates that, over the *p*H range investigated, iron

[3] Vacuum Metals Corporation.

is approximately 200 mv more active than a reversible hydrogen electrode in the same solution.

Corrosion rates.—Corrosion rate determinations for pure iron as a function of *p*H are shown in Table I. Duplicate runs at *p*H 0.96, conducted at different times with different specimens, illustrate the reproducibility attained. In all these tests *p*H of the solution was maintained essentially constant. In order to do this for the run at *p*H 4, where the difficulty was greatest, it was necessary to increase the volume of the solution to 5.5 l. It is evident that the corrosion rate does not vary significantly over the *p*H range 1–4 in deaerated solutions, the value ranging from 29 mdd at *p*H 1 to 25 mdd at *p*H 4. Gemmel (7) reports similar behavior for mild steel in the same environment. The effect in aerated solutions is very much larger (8).

It is no longer practical to measure corrosion rates by iron analysis in deaerated solutions of *p*H greater than about 4, because the volume of solution necessary to maintain a constant *p*H becomes extremely large, and insoluble corrosion products form on the surface.

Concentration polarization.—Cathodic polarization measurements were then conducted to determine the variation of hydrogen overvoltage with *p*H. Fig. 3 summarizes the results obtained. Instead of a complete linear relation between potential and the logarithm of current density in accord with the Tafel relations, only portions of the various curves exhibited this behavior. Sharp breaks, dependent on *p*H, were observed at critical values of current density measurements, after which the curves approached one common straight line. Various interpretations of such breaks have been offered recently (9) but their origin can be shown to result from concentration polarization.

This can be proved by the following sequence of reasoning and experiment. At a surface where hydrogen ions are being removed to form hydrogen gas, more ions reach the surface by three distinct mechanisms: (*a*) diffusion from the bulk of the solution, (*b*) migration under the influence of the existing electric field, and (*c*) convection caused by stirring which brings fresh solution to the metal surface. Of these three, only the first is of major significance, since the solution was not stirred, and the transference number of hydrogen ions in 4% sodium chloride is negligible. (The major current is carried by Na^+ and Cl^-.) Therefore, the limiting diffusion current for hydrogen ions can be calculated with the aid of the following equation derived from Ficks' First Law (10, 11):

$$i_L = \frac{nFD}{\delta}(10^{-3})a_{H^+} \qquad \text{(I)}$$

TABLE I. *Corrosion rate of pure iron in oxygen-free 4% NaCl as a function of pH at 25°C*

pH	Corrosion rate (mdd)
0.96	29.7
0.96	27.6
2.0	28.2
2.91	29.3
3.96–4.03	25.0

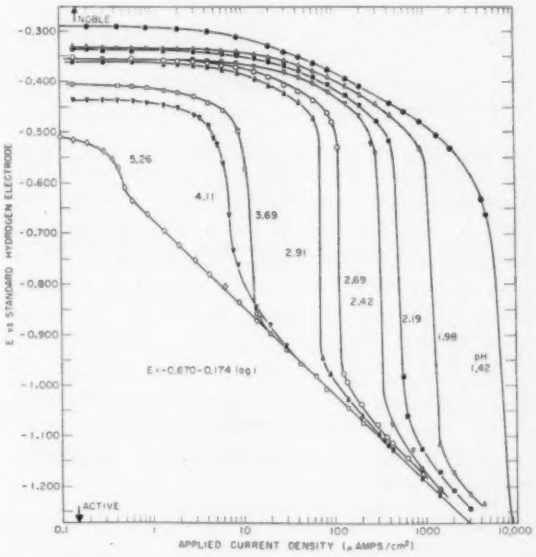

FIG. 3. Effect of *p*H on the cathodic polarization of pure iron in deaerated 4% NaCl.

where i_L = limiting diffusion current (amp/cm²), n = number of electrons taking part in the reaction, $\mathbf{F}$ = Faraday constant, δ = thickness of the diffusion layer (cm), a_{H^+} = activity of hydrogen ions (moles/liter), D = diffusion coefficient for H^+ (cm²/sec). With D equal to 7.39 (10^{-5}) cm²/sec (12) and δ equal to 0.05 cm (13),

$$i_L = 0.143\, a_{H^+} \qquad \text{(II)}$$

$$\log i_L = -0.845 - p\text{H} \qquad \text{(III)}$$

Therefore, the logarithm of the limiting diffusion current is expected to vary in a linear manner with *p*H.

The calculated expression for this variation (equation III) is given in Fig. 4, together with the experimental determination of the limiting diffusion current found at various *p*H values. Deviation from a straight line relation at low *p*H values is expected because of the stirring effect of hydrogen gas liberated in greater quantities at the higher current densities. Stirring reduces the stagnant film thickness, δ, and introduces the factor of convection which has been neglected in the above derivation. A high trans-

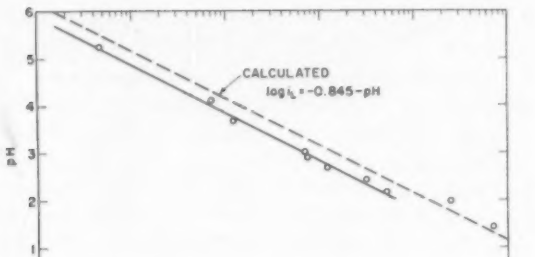

FIG. 4. Effect of *p*H on the limiting diffusion current for hydrogen ions in 4% NaCl.

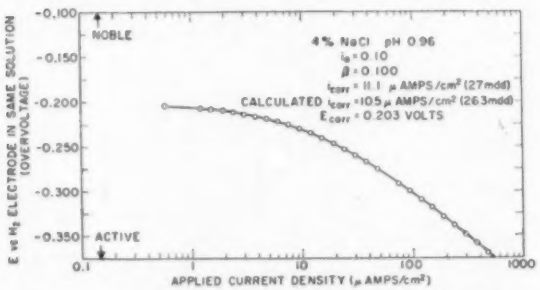

FIG. 5. Hydrogen overvoltage (activation) on pure iron in 4% NaCl at *p*H 0.96.

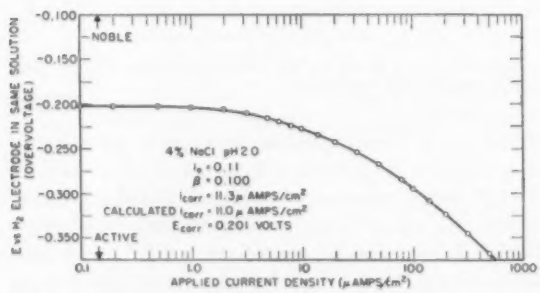

FIG. 6. Hydrogen overvoltage (activation) on pure iron in 4% NaCl at *p*H 2.0.

ference number for hydrogen ions at the lower *p*H values would also cause higher limiting diffusion currents. Agreement between equation (III) and the experimental values is convincing proof that deviations from the Tafel relation may be caused by concentration polarization of hydrogen ions. This important factor has sometimes been overlooked in interpretation of reported data on polarization and overvoltage; yet, the actual potential change introduced by concentration polarization can be greater than that from any other source. In addition, the indiscriminate use of surface roughness factors for calculating current densities is inconsistent with the concept of concentration polarization since δ would not be affected by very small surface irregularities.

Further simple experimental evidence that the breaks in the cathodic polarization measurements of Fig. 3 are caused by an increase in *p*H at the iron surface was obtained by introducing phenolphthalein into the solution, and observing a red color formation on the electrode surface at current densities corresponding to the rapid change of slope.

Behavior above the limiting diffusion current.—The above experiments clearly show that attempts at measurement of activation overvoltage in sodium chloride solutions above *p*H of about 2 are liable to include an appreciable contribution because of concentration polarization. The common linear overvoltage relation found for all the hydrogen ion concentrations above their respective limiting diffusion currents may be explained by assuming that the the limiting *p*H produced at the surface is the same in all the solutions. The value of this limiting *p*H is not known precisely, but probably approaches values of 12–14 (14, 15). Above the limiting diffusion current the predominant reaction presumably changes from reduction of hydrogen ions to the direct reduction of water (14, 16), accompanied by a high *p*H at the electrode surface. This change in mechanism appears quite reasonable, since Delahay (14) has shown that dissociation of water is too low to account for the experimental current densities used in generation of hydrogen in neutral and alkaline media. Also the discharge of water has been established for copper in solutions of high *p*H by Bockris and Pentland (17).

Since the actual *p*H at the electrode surface is not known precisely, the linear relation found in Fig. 3 cannot be justifiably expressed in terms of overvoltage (potential vs. a hydrogen electrode in the same solution), and a reference electrode scale which is independent of *p*H must be used; therefore, using a modified expression of the Tafel relation

$$E_H = A - \beta \log i \qquad \text{(IV)}$$

where E_H = potential on standard hydrogen scale, A and β are constants, and i = current density ($\mu a/cm^2$).

The experimental results for reduction of water on an iron surface follow the relation

$$E_H = -0.670 - 0.174 \log i \qquad \text{(V)}$$

Activation overvoltage and corrosion rate calculation.—Cathodic polarization measurements at current densities low enough to avoid concentration polarization are shown for pure iron in 4% sodium chloride at *p*H 0.96 and 2.0 in Fig. 5 and 6. The curves are essentially horizontal at the low current densities and exhibit the Tafel relationship only at higher values of applied current. The relation be-

tween hydrogen overvoltage (activation polarization) and current density may be expressed (18):

$$\eta_a = -\beta \log \frac{i}{i_o} \qquad \text{(VI)}$$

where η_a = hydrogen (activation) overvoltage or potential measured against a hydrogen electrode in the same solution, β = constant (the slope of the Tafel region), i = total cathodic current density, and i_o = exchange current density or the current equal to the equilibrium rate of hydrogen reduction at the reversible hydrogen potential.

Equation (VI) may be applied both for an iron or a platinum electrode; however, iron, unlike platinum, does not function as a reversible hydrogen electrode when no external current is impressed. This is true primarily because iron corrodes (local action current flows) and one may consider the iron potential as that of a hydrogen electrode polarized cathodically in accord with equation (VI). When a cathodic current is impressed on a corroding metal it becomes evident that i, the total cathodic current density in equation (VI), should be replaced by the sum of two separate current density terms; i_x, the externally applied cathodic current and i_{la}, the local action current. The two are obviously not independent since the principle of cathodic protection is based on the reduction of i_{la} with an increase of i_x. From what has been described above, equation (VI) may be written in a more general form:

$$\eta_a = -\beta \log \frac{i_x + i_{la}}{i_o} \qquad \text{(VII)}$$

Equation (VII) is consistent with the horizontal portion of the experimental curves, since it predicts that the potential will not change significantly until the external current approaches values of the same order of magnitude as the local action current. This is in accord with observations.

It is important to note that with no external applied current ($i_x = 0$), η_a equals the corrosion potential, E_{corr}, on the hydrogen overvoltage scale, and i_{la} equals the corrosion current, i_{corr}; hence,

$$E_{corr} = -\beta \log \frac{i_{corr}}{i_o} \qquad \text{(VIII)}$$

Equation (VIII) may be used to calculate the corrosion current if β, i_o, and the corrosion potential are known. The slope β is determined graphically from the Tafel region of a cathodic polarization measurement. The exchange current is determined by extrapolation of the Tafel region to the reversible hydrogen potential.

The rate determined by iron analysis and that calculated with equation (VIII) are tabulated in Fig. 5 for iron in 4% sodium chloride at *p*H 0.96 and in

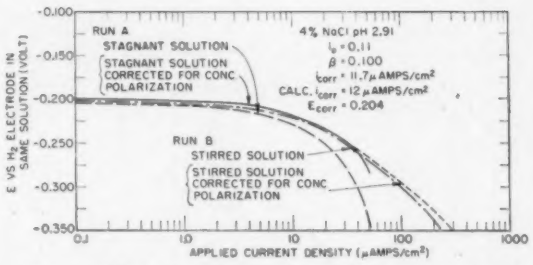

FIG. 7. Effect of stirring on concentration polarization of pure iron in 4% NaCl at *p*H 2.91.

Fig. 6 for a *p*H of 2.0. The two methods agree within experimental error.

The above-described electrochemical method cannot easily be applied at higher *p*H values because of the interference of concentration polarization on the determination of β and i_o; however, Fig. 7 shows cathodic polarization measurements conducted at *p*H 2.91 with and without stirring. Stirring tends to eliminate concentration polarization in a manner already discussed. This figure shows that the limiting diffusion current with the stirring rate used is about ten times that in a stagnant solution. The dependence of concentration polarization on current density can be expressed as (10):

$$\eta_c = 0.059 \log \frac{i_L - i}{i_L} \qquad \text{(IX)}$$

where η_c = concentration polarization, and i_L = limiting diffusion current density.

Although equation (IX) has been shown to provide only approximate agreement with experiment when i approaches i_L (16), it can be used to correct the experimental data of Fig. 7. Such correction leads to a short linear portion of the activation overvoltage curve at *p*H 2.91. Values of the overvoltage constants and calculated and experimentally determined corrosion rates are tabulated in this figure.

It is of interest to compare the behavior of pure iron in sodium chloride solutions with that in other environments because of the influence of other anions, particularly as complexing agents for ferrous ions; therefore, measurements were conducted in 0.1*M* citric acid (*p*H 2.06) and 0.1*M* malic acid (*p*H 2.24). Fig. 8 shows overvoltage measurements in these media along with the calculated and measured corrosion currents. It is important to note that β values in these media are somewhat different from the value found for sodium chloride. In addition, there is an effect of environment on the exchange current, i_o, the values being 1×10^{-1} μa/cm² in 4% sodium chloride, 9.3×10^{-2} μa/cm² in 0.1*M* citric acid, and 1.5×10^{-2} μa/cm² in 0.1*M* malic acid.

Agreement between electrochemical calculation

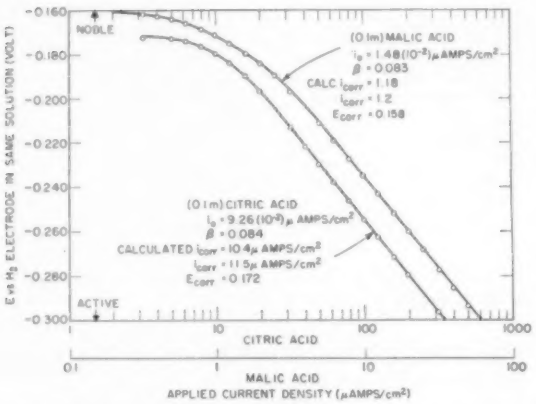

FIG. 8. Hydrogen overvoltage (activation) on pure iron in 0.1*M* citric acid and 0.1*M* malic acid.

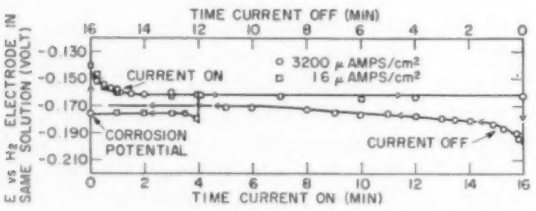

FIG. 9. Effect of time on the potential of pure iron in 0.1*M* citric acid after anodic currents of 16 and 3200 μa/cm^2 were applied, then stopped.

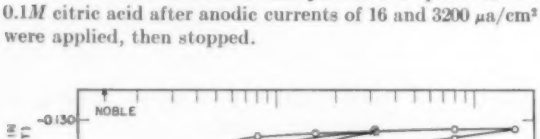

FIG. 10. Typical hysteresis phenomenon observed during anodic polarization of iron in acid media. Curves obtained in 0.1*M* citric acid by alternately increasing and decreasing the anodic current.

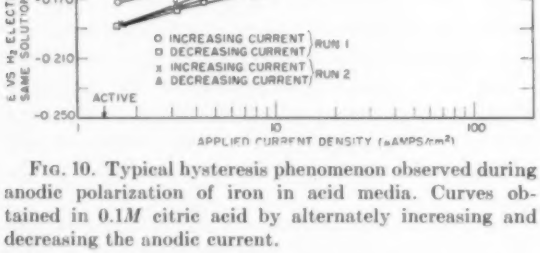

FIG. 11. Typical anodic polarization measurements for iron in various acid media.

and experimental determination of corrosion current is important because it indicates the existence of a very large cathode-to-anode area ratio. This is true since the constants used in the electrochemical calculation were determined in a current region where the specimen would be expected to function entirely as a cathode. The concept of a very large cathode-to-anode area ratio already has been expressed independently by Uhlig (5) and Hoar (19) for iron in acid environments.

Anodic polarization behavior.—Anodic polarization behavior is much more complex than cathodic behavior. Anodic measurements were not as reproducible, exhibiting marked hysteresis depending on whether current was increasing or decreasing. In addition, such measurements were dependent both on time at a given current density and on the arbitrary current density increments used. Time dependence is illustrated in Fig. 9 which shows how the potential of a pure iron electrode in 0.1*M* citric acid changes with time at anodic current densities of 16 μa/cm^2 and 3200 μa/cm^2. When anodic current is applied, the potential changes sharply to a more noble value, then drifts slowly in the active direction. When the current is shut off, the reverse situation occurs. The potential drops to a more active value, then slowly drifts in the noble direction. In addition, after anodic current shutoff, the potential of the iron specimen is more noble than its original steady-state value, and several hours are required before the potential assumes its original value.

The hysteresis phenomenon previously referred to is illustrated in Fig. 10 which shows anodic polarization measurements in 0.1*M* citric acid obtained by increasing and decreasing the applied current a number of times. It is evident that increasing anodic current yields an entirely different curve from decreasing current. Anodic polarization measurements were taken allowing 2–4 min between current increments.

Fig. 11 contains typical anodic polarization measurements conducted in a variety of media. It is apparent that iron does not polarize significantly at the higher anodic current densities. The anodic measurements illustrated should be considered as only typical of the general shape of the many curves actually obtained for reasons discussed later.

DISCUSSION

Cathodic polarization measurements on pure iron in 4% sodium chloride indicate that the activation overvoltage constants for reduction of hydrogen are essentially independent of *p*H, i_o being approximately 0.1 μa/cm^2, and β having a value of 0.100.

From what has already been discussed, it becomes

obvious that the equation for local cathodic polarization in this medium may be expressed:

$$\eta_a + \eta_c = -\beta \log \frac{i}{i_o} + 2.3 \frac{RT}{n\mathbf{F}} \log \frac{i_L - i}{i_L} \quad \text{(X)}$$

for situations where i, the total cathodic current, is less than i_L.

This may be extended to give the more general equation:

$$\eta_a + \eta_c = -\beta \log \frac{i_z + i_{la}}{i_o} + 2.3 \frac{RT}{n\mathbf{F}} \log \frac{i_L - i_z - i_{la}}{i_L} \quad \text{(XI)}$$

or

$$E_H = -0.059p\text{H} - \beta \log \frac{i_z + i_{la}}{i_o} + 2.3 \frac{RT}{n\mathbf{F}} \log \frac{i_L - i_z - i_{la}}{i_L} \quad \text{(XII)}$$

When the total current appreciably exceeds i_L, equation (XII) becomes equation (V).

With a knowledge of the limiting diffusion current as a function of pH, β, and i_o, a family of *local* cathodic polarization curves may be drawn for iron in 4% sodium chloride as presented in Fig. 12. Combining this series of local cathodic polarization curves with the observed facts that the corrosion potential varies by 0.0559 v for each pH unit change and the corrosion current is essentially constant over the pH range 1–4, it is concluded that the local anodic polarization curve for iron at currents corresponding to the corrosion current is extremely steep. This is also consistent with the concept of a very large cathode-to-anode area ratio since even small currents would yield high current densities at a small area and, therefore, cause marked polarization.

The anodic behavior of iron can probably best be explained as follows. At high applied current densities, the major portion of the iron surface functions as anode, whereas only a small fraction is anode without external applied current. A sluggish shift in the anode-to-cathode area ratio (18), as anodic current is applied, is sufficient to explain both the time dependence and hysteresis phenomena observed. The difficulty in reproducing anodic curves and their marked dependence on experimental methods indicate that a more quantitative discussion of the measurements would at best lead to very uncertain conclusions. The necessity for more research to improve the present understanding of basic anodic polarization phenomena was amply demonstrated in this work.

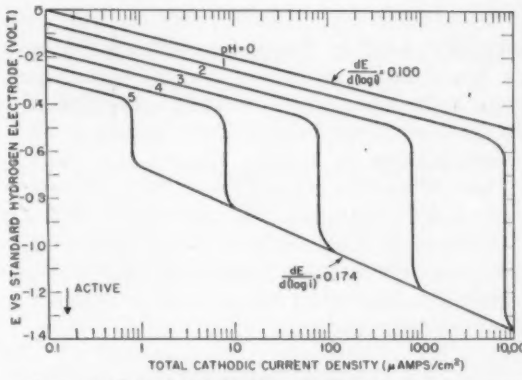

FIG. 12. Calculated local cathodic polarization curves for pure iron in deaerated 4% NaCl at various pH values.

Pure iron, in the acid environment discussed, corrodes uniformly in the sense that no pitting or intergranular attack occurs; however, there appears to be a marked effect of orientation. After a prolonged corrosion test, certain crystal faces are attacked more than others, the net result being that some faces appear to protrude from the surface. The electrochemical measurements presented here therefore must be considered as average values for random orientation. The marked effect of orientation indicates that there is a significant variation of the overvoltage constants for different crystal orientations.

The electrochemical calculation of corrosion rate is certainly not universally applicable because of its many limitations. The most important of these are the necessity for complete absence of any depolarizer, and the necessity for elimination of concentration polarization and resistance potential drops in the measurements. Although resistance polarization was not important in the cases discussed here because of the low currents and high conductivity used, an illustration of its interference will be demonstrated in a later publication which discusses application of the method to the testing of alloys. The resistance polarization became important because the corrosion current of one alloy was so high that considerable external current was required to polarize the material up to the Tafel region. [See equation (VII).] This gave some difficulty from the point of view of both resistance and concentration polarization behavior. As already indicated, concentration polarization alone is sufficient to interfere with the method above a pH value of about 3. Indeed, above about pH 5 the local action current alone appeared to be sufficient to bring the specimen into the concentration polarization region, causing a pH increase at the surface.

A further requirement of the method is that the environment be such that platinum functions as a

hydrogen electrode; in addition, the metal used must not exhibit passivity phenomena in the environment, nor should the metal have any insoluble surface films which are reduced by the cathodic current; finally, the surface should exhibit Tafel hydrogen overvoltage behavior.

The work of Wagner and Traud (20) and Bockris (21) is most important in the development of many of the concepts described here. Consideration of the ideas presented by these investigators will lead undoubtedly to marked advances in the understanding of corrosion mechanisms.

Acknowledgment

This program was supported by a Post-Doctoral Fellowship established by the Weirton Steel Company. The discussions and guidance of Professor H. H. Uhlig were invaluable throughout the course of the work.

Any discussion of this paper will appear in a Discussion Section to be published in the June 1956 JOURNAL.

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Some Properties of Tin(II) Sulfate Solutions and Their Role in Electrodeposition of Tin

III. Solutions with Tin(II) Sulfate, Sulfuric Acid, and Addition Agents[1]

C. A. Discher

Rutgers University, The State University of New Jersey, College of Pharmacy, Department of Chemistry, Newark, New Jersey

ABSTRACT

Density, refractive index, surface tension, viscosity, freezing point, conductivity, transference numbers, and electrode potentials were measured for tin(II) sulfate-sulfuric acid solutions containing addition agents. The addition agents were selected to give a range of deposit types.

Solutions were classified as to the deposits obtained from them. Specific properties of each solution were studied to determine the correlation between deposit type and the magnitude of a given property. Molar refraction, equivalent conductance, surface tension, and van't Hoff's i were found to have a well-defined relationship to deposit type. Transference and viscosity show some correlation to deposit. The other properties show no correlation.

Findings are critically analyzed in an attempt to reveal the nature of the cathode processes.

Introduction

Some physical properties of aqueous tin(II) sulfate and tin(II) sulfate-sulfuric acid solutions have been reported previously (1, 2). In the present paper the same properties are reported for a series of tin(II) sulfate-sulfuric acid solutions containing addition agents. The data have been critically analyzed in order to determine the role of each property in the deposition of tin at the cathode.

Experimental

The procedures and equipment used for this work have been described (1). However, because of the relatively large freezing point depressions of the solutions studied, a differential thermometer could not be used. A low temperature thermometer graduated in 0.1°C divisions was substituted. Nitrogen atmospheres were not used with those solutions which previous experience had shown to be relatively insensitive to air oxidation for the periods of time needed to conduct the measurements.

The solutions were prepared to give tin(II) sulfate and sulfuric acid concentrations of approximately 100 g/l each, the exact composition being determined analytically. This is a ratio of approximately one mole of tin(II) sulfate to slightly more than two moles of sulfuric acid, which was the ratio most thoroughly investigated before (2). This concentration also made it possible to draw upon previous work with addition agents in tin(II) electrolytes of similar concentrations.

The addition agents were selected to give electrodeposits of widely different characteristics, ranging from bright deposits to uncontrolled masses of needles and trees. Some of the addition agents used, e.g., cresol, β-naphthol, and animal glue, are well known (3). Others, e.g., eugenol, 8-hydroxyquinoline, quinoline, n-octyl alcohol, o-toluidine, Carbowax-1500[2], Tergitol-7, were reported by Mathers and Discher (4). Still others, e.g., amylene (saturated), n-butyl alcohol (30 g/l), n-butylamine (1 g/l), butyl carbitol (10 g/l), benzyltrimethylammonium hydroxide (1 g/l), dimethylsulfolane (5 g/l), dithiobiuret (1 g/l), ethyl methyl ketone (80 g/l), mannitol (30 g/l), methyl cellulose (saturated), and sodium p-cymene sulfonate (1 g/l), were selected from unpublished experiments performed in Mathers' laboratory[3] and in this laboratory. Addition agents used to give bright deposits, i.e., wood tars and n-aliphatic alcohol sulfates, have been reported (5). The substances listed were used singly or in combinations to give a total of 32 different electrolytes for study. Plating samples were prepared as previously described (1).

Results

Deposit types.—Tin deposits obtained from the various solutions studied were classified into five

[1] Manuscript received June 28, 1954. This paper was prepared for delivery before the Chicago Meeting, May 2 to 6, 1954.

[2] Carbide and Carbon Chemicals Company, New York, N. Y.

[3] Indiana University, Bloomington, Indiana.

TABLE I. *Classification of deposits and the symbols used for each classification*

Type	2-dimensional	3-dimensional	Description of deposit
I	Open circle	Light sphere	Bright
II	Blackened circle	Dark sphere	Matte
III	Dot in circle	Cube	Crystal growth well controlled, but surface rough or visibly grainy in appearance.
IV	Open triangle	Pyramid	Surface crystal growth controlled as in Type III, but poor control of crystal growth from the edges and corners.
V	Blackened triangle	Pyramid	No control of crystal growth from either edges, corners, or surface. Deposit a mass of needles or trees.

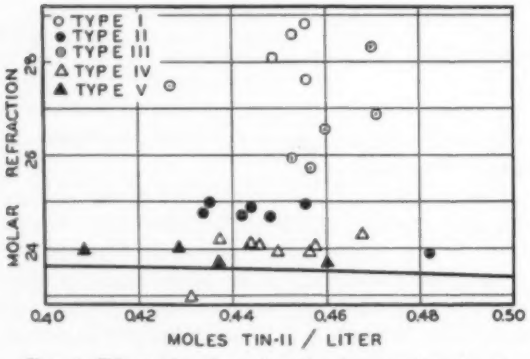

FIG. 1. Effect of molar refraction in grouping the electrolytes studied according to the type of deposit obtained. The molar refraction of corresponding solutions without addition agents is represented by the heavy line.

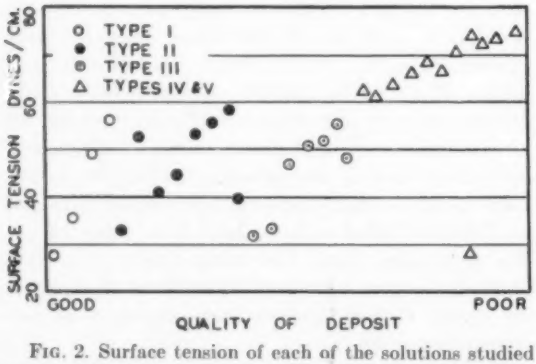

FIG. 2. Surface tension of each of the solutions studied arranged in the order of the deposit quality. The solution giving the brightest deposit is on the extreme left and the poorest on the extreme right.

types. The characteristics of each type together with the symbol used to represent it in the figures are presented in Table I. These classifications are based on visual examination. In some cases it was difficult to judge to which of two classifications a given deposit belonged. It is interesting that in these cases the plotted points also fall in the borderline regions.

Essentially the five types may be further classified into only two groups, those deposits in which crystal growth from the edges and corners is restrained and controlled, Types I, II, and III, and those in which there is no control of crystal growth from the edges and corners, Types IV and V. It should be pointed out that in some of the plots presented, Type V deposits are not distinguished from Type IV.

Except for surface tension data the results obtained are not presented as raw experimental data. Since the concentration of tin(II) sulfate varied slightly among the different solutions, it was necessary to compensate for this variation by presenting the data on a molar or equivalent basis. For example, refractive index data is presented as molar refraction.

Refractive index.—The results are presented in Fig. 1 as a plot of molar refraction against concentration of tin(II) sulfate. The molar refraction is based upon the tin(II) present with appropriate corrections applied for the contributions to the refractivity by the sulfuric acid and the addition agent. It is clear from this plot that those solutions capable of producing bright deposits (Type I) have comparatively high molar refractions, while those which yield completely uncontrolled deposits (Type V) have molar refractions approximating those for similar tin(II) sulfate-sulfuric acid solutions without addition agents. Type IV deposits are obtained from solutions whose molar refraction varies only slightly from solutions without addition agents. Molar refractions for deposits of Types II and III fall in separate areas between Types I and IV.

It is also evident from this figure, as from subsequent figures, that variation of tin(II) concentration within the range 0.4–0.5M does not affect deposit type.

Surface tension.—Fig. 2 gives the surface tension of the solution in relation to quality of deposit. This property separates the solutions studied into two categories, (*a*) those which control edge crystal growth (Types I, II, and III), and (*b*) those which do not (Types IV and V). The limiting surface tension is apparently 60 dynes/cm, with controlled deposits being obtained from solutions having lower surface tensions. However, values of less than 60 for this property do not insure deposit control since one electrolyte had a surface tension of 29 dynes/cm but showed no control of edge crystal growth. On the other hand, no solution with a surface tension greater than 60 was found which could control crystal growth from the edges and corners of the cathode.

Conductance.—Equivalent conductances at in-

finite dilution are presented in Fig. 3 as a plot against the concentration of tin(II). The Onsager equation was used for the calculation, which is based on the total equivalents of electrolyte [tin(II) sulfate plus sulfuric acid] present in the solution. Calculations using equivalents of tin(II) give similar distributions of points when plotted, as do experimental equivalent conductances.

This property groups the solutions into three general regions in the graph. Those solutions giving Type IV and V deposits usually have equivalent conductances appreciably higher than corresponding solutions without addition agents, while those giving Type III deposits show appreciably lower values of this property. Solutions giving Type I and II deposits fall between and generally have equivalent conductances approximating those for corresponding solutions without addition agents.

Freezing point depression.—van't Hoff's i was calculated for each solution, and the following regularities were noted. All values of i fall between 1.6 and 2.0. Solutions giving Type III deposits are well grouped, with values between 1.6 and 1.8. Solutions giving Type IV and V deposits have i values between 1.8 and 1.9, approximating those for corresponding solutions without addition agents. Types I and II generally have i values greater than 1.9 but the picture is not as clear since in a few cases the i value falls within the range for Types IV and V.

Viscosity.—There is a tendency for the points representing each of the solutions to arrange themselves according to deposit. However, the boundaries between the areas are diffuse due to overlapping.

Transference numbers.—Experimental transference numbers for these solutions appeared confusing at first glance. Determinations were made for both the anode and cathode compartments in the hope that checks would be obtained. Those solutions which gave concordant results for both compartments were few indeed. Usually differences were much greater than experimental error. Continued study of the experimental data, however, showed several regularities. This would seem to indicate that the differences are real in solutions of the concentrations used in this study. Unless otherwise specified, average values for transference are used.

Solutions giving Type I or II deposits have transference numbers for tin(II) of either about 0.10 or 0. They range around zero for Type III deposits. Solutions giving Type IV or V deposits have tin(II) transference values in the range 0.04–0.07. The relative sign for the tin(II) transference numbers with respect to each compartment is extremely interesting. For the bright and matte deposits (Types I and II) the cathode transference numbers are usually smaller, i.e., more negative, than the anode transference numbers. For Type III the cathode

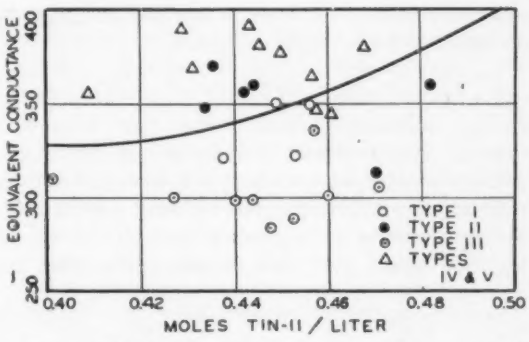

FIG. 3. Effect of equivalent conductance in grouping the electrolytes studied according to the type of deposit obtained. The equivalent conductance of corresponding solutions without addition agents is shown by the heavy curved line.

value was always positive with respect to the anode value. The Type IV and V values were about equally divided in this respect.

Values for hydrogen transference ranged from 0.80 to 1.05. With only five exceptions, cathode values were smaller than corresponding anode values. This seems to indicate some hydrogen deposition and occlusion despite the relatively low current used for these measurements (*ca.* 10 ma).

Another interesting regularity noted is the ratio of the transference by hydrogen (n_{H^+}) with respect to total transference by hydrogen and tin(II) ($n_{H^+}+n_{Sn^{++}}$). This fraction is 1.00 for the Type I and III deposits and 0.90 for the matte deposits. On the other hand, values for Type IV and V deposits ranged from 0.93 to 0.95, with the average value of 0.94.

Electrode potentials.—Experimental values obtained for the potentials of the hydrogen electrode and the tin electrode, respectively, vs. the n-calomel electrode fail to show any pattern with respect to the plating properties of the solutions studied; neither do activities or activity coefficients calculated on the basis of these experimental results. A variation by which activity and activity coefficients were plotted against ionic strength instead of concentration also failed to show any regularities.

The solutions were all of pH less than 1. This, together with the fact that reducible organic substances were present in most solutions, may account for failure of plating properties to correlate with hydrogen ion activity.

It is also possible that the organic compounds interfered with the process at the tin electrode. Roth and Leidheiser (6) showed that, in the case of nickel solutions, concentration of addition agent is a factor in the value of the electrode potential. This factor was not controlled in the work presented in this paper, the concentration of addition agent being

selected solely on the basis of the plating sample to be obtained from the electrolyte.

Discussion

The following generalizations may be drawn directly from the work as presented to this point. First, those electrolytes whose properties (other than equivalent conductance) most closely approximate the properties of corresponding electrolytes without addition agents give poor deposits. (Electrode potentials must be omitted since no correlations were observed.) Second, in determining deposit type, failure to control crystal growth at the edges of the cathode was frequently more important than the nature of the surface growth. This is especially apparent in the case of surface tension.

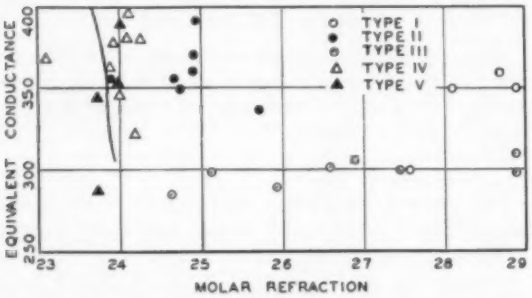

Fig. 4. Effect of both equivalent conductance and molar refraction in grouping the electrolytes studied according to the type of deposit obtained. Corresponding solutions without addition agents are represented by the curved line.

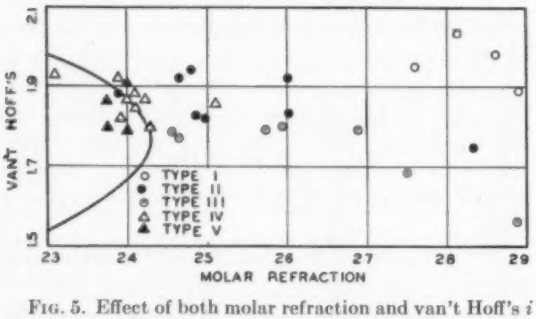

Fig. 5. Effect of both molar refraction and van't Hoff's i in grouping the electrolytes studied according to type of deposit obtained. The curved line represents these properties for solutions without addition agents.

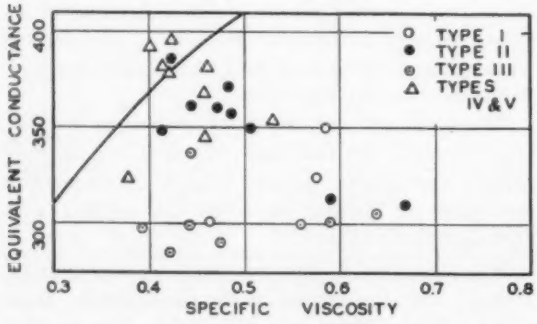

Fig. 6. Effect of equivalent conductance and specific viscosity in grouping the electrolytes studied according to the type of deposit obtained. Corresponding solutions without addition agents are represented by the curved line.

When properties are plotted against molar concentration of tin(II), it is observed that there are points in each of the plots which apparently do not fit into the general pattern. Since tin(II) concentration is not important within the range of concentrations used, it was necessary to resort to other means to determine whether these points were significant variants or were merely the result of the use of a nondeterminant [tin(II)] as one of the axes. The data were therefore studied by means of a series of graphs in which all possible pairs of properties were used as variables. Fig. 4–6 are representative of this study; others could do equally well. Fig. 6 does not show good separation of points, but it is presented to show the role of viscosity. Specific viscosity, while important to some extent, does not separate the deposit types as effectively as some of the other properties, e.g., molar refraction. In Fig. 4 and 5 it is apparent that the number of points falling outside the area in which similar points are found have been greatly reduced, as compared to those figures in which tin(II) concentration was used as one of the axes.

Three dimensional plots were next attempted. Fig. 7 shows this type of plot using equivalent conductance, molar refraction, and van't Hoff's i as the variables. Each point falls into a volume occupied only by points representing similar deposits. There are no exceptions. Fig. 8 is based on Fig. 7. The planes approximate the boundaries between the volumes occupied by the points representing a given deposit type.

A similar plot, not shown, substituting Macleod's constant for van't Hoff's i gives similar results. Even the point for the solution having a surface tension of 29 dynes/cm, but giving a poor deposit, is within the volume occupied by points which represent solutions giving similar deposits.

From these studies it is evident that molar refraction, equivalent conductance, surface tension, and van't Hoff's i are definitely related to the type of deposit obtained from a given electrolyte. Transference data suggest the involvement of this property. Viscosity is a factor, but not as sharply defined in its effect. To obtain a given type of tin deposit each of these properties must have values within a limited range. For example, if a solution could be tailored to have a molar refraction of 28, a surface tension of 35, a van't Hoff's i of 3.95, and an equiv-

alent conductance of 340 (all in conventional units), it should give bright deposits of tin.

While all measurements made represent properties of the body of electrolyte they do throw some light on the electrode process involved in tin deposition. The following discussion indicates how the properties which were shown determinants of deposit type may modify the cathode environment or film.

Equivalent conductance.—Since there is no visible hydrogen evolution under the conditions used to prepare plating samples, it must be assumed that diffusion of tin(II) into the cathode reaction area is not a limiting factor for the deposition rate in these baths. It therefore follows that conductance is a measure of the rate at which the primary electrode process may proceed, since the rate at which electrons become available at the cathode is limited by conduction through the solution. Apparently the reduction rate is quite critical since the bright and matte deposits have equivalent conductivities intermediate between the Type III and the Type IV and V deposits. It may be said that values of equivalent conductivity between 325 and 375 represent conductivities which allow the optimum rate of transfer of electrons to the tin(II) ions. van't Hoff's i would also be expected to group the deposits, since it is a measure of the number of particles available to conduct the current in the solution.

Surface tension.—Substances which lower surface tension concentrate in the interfacial film. Since all effective addition agents for this bath lower the surface tension below 60 dynes/cm, it follows that the interfacial film at the cathode surface must be richer in addition agent than is the body of the electrolyte. Since a uniform electrical field is essential for a smooth deposit (6), it seems possible that effective addition agents concentrate sufficiently in the cathode film to insure or at least aid in establishment of a uniform field and thus prevent excessive crystal growth from the otherwise high current density areas at the edges and corners of the cathode.

Surface tension properties must also be involved in the modification of the cathode film in still another way. Electrolytes tend to increase surface tension and to concentrate in the body of the solution, leaving the interfacial film less concentrated in their respect. It has previously been shown that tin(II) sulfate and tin(II) sulfate-sulfuric acid solutions (without addition agents) have higher surface tensions than water (1, 2). This means that the cathode film is depleted in tin(II) not only because of the electrode reaction, but its concentration in tin(II) is normally lower than that determined for the body of the electrolyte because of this tendency for ionic substances to concentrate in the body of the solution. Due to these negative concentration gradients, the complex sulfatostannite ion of the body of the solution must be degraded to a large extent into simpler particles, especially neutral molecules, since the existence of the complex is dependent on concentration.

Viscosity.—This property would modify the rate at which ions can approach the cathode, but on the basis of this work the property is not as important a determinant of deposit type as molar refraction, equivalent conductance, or surface tension.

Molar refraction.—The refractive index measurements were made relative to the D-line of sodium.

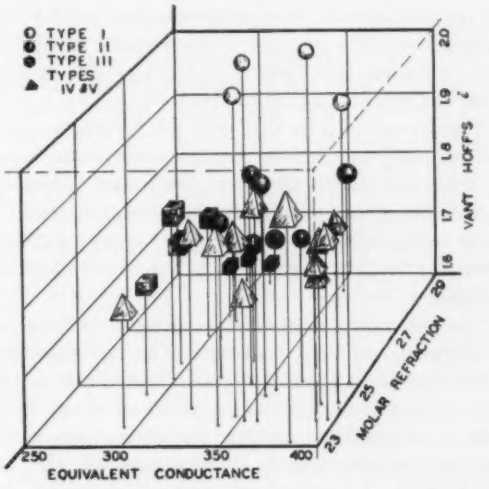

FIG. 7. Effect of equivalent conductance, molar refraction, and van't Hoff's i in grouping the electrolytes studied according to the type of deposit obtained.

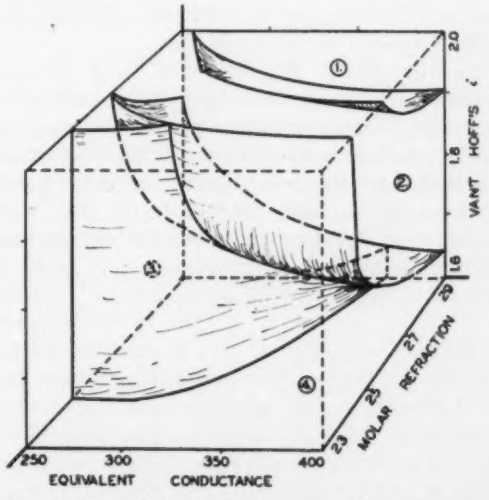

FIG. 8. Approximate volumes occupied by points representing the properties, equivalent conductance, molar refraction, and van't Hoff's i for the solutions studied. The numbers correspond to the deposit type except that the deposit types IV and V both fall in volume 4.

Therefore, it may be said that the molar refraction, as calculated, represents the distortion or deformability of the electron shell of the tin(II) (electron polarizability). The conclusion drawn is that increased polarizability of the tin(II), whatever its form in the cathode film, favors increased control of deposit, since molar refractions of all solutions which show controlled crystal growth are greater than those of solutions which do not. As the tin(II) unit moves into the field surrounding the cathode, increased polarizability would affect its behavior in the cathode film. On reaching the cathode surface the tin(II) unit must be oriented so as to present its positive pole to the negatively charged cathode; presumably the enhanced electrostatic attraction thus afforded facilitates the transfer of electrons from the cathode to the tin(II) unit.

Transference.—The fact that the hydrogen transference, as measured in the cathode compartment, is relatively more negative than that measured in the anode compartment would seem to indicate some reduction of hydrogen ion at the cathode. However, hydrogen gas was never observed at the cathode.

The constancy of the ratio between transference by hydrogen to total transference by hydrogen and tin(II) for given deposit types indicates that a definite ratio of hydrogen to tin(II) is essential. However, since tin(II) transference numbers are small, zero, or slightly negative, it seems probable that the net cathode process must be kinetic diffusion of tin(II) toward the cathode film. In light of the discussion under surface tension, the unit diffusing into the cathode film should be tin(II) sulfate molecules. This would be aided by the induced dipoles, indicated in the discussion of molar refraction.

Recently, Finch, Wilman, and Yang (7) summarized the factors influencing crystal growth at the cathode. Of these, (*a*) rate of arrival of metal ions, and (*b*) uniform concentration of the electrostatic field at the cathode surface, are substantiated for the tin(II) sulfate-sulfuric acid bath by this work. (Another point, atomic arrangement of the substrate surface, was essentially a constant for the purposes of the present paper.) However, in the light of this new work it is necessary to include polarizability of the metal unit as a determining factor.

Conclusions

It was found that the cathode deposit obtained from tin(II) sulfate-sulfuric acid electrolytes is clearly related to the surface tension, molar refraction, van't Hoff's i, and equivalent conductance of the solution. Viscosity and the ratio of transference by hydrogen to total transference were also factors, but less clearly so.

In terms of the cathode process, the data indicate that increased polarization favors better deposits. There is a preferred rate of reduction at the cathode, which is a function of equivalent conductance. Surface tension must be below 60 dynes/cm for good deposits. Transference data indicate that for a good deposit, hydrogen is for practical purposes the sole carrier of the current in the electrolyte, and that the tin(II) migrates into the cathode film by diffusion rather than by conduction.

Acknowledgment

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1956 Journal.

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Separations with a Mercury Electrode

Determination of Certain Metallic Impurities in Vanadium Salts[1]

WILLIAM E. SCHMIDT[2] AND CLARK E. BRICKER

Princeton University, Princeton, New Jersey

ABSTRACT

By means of electrolysis with a mercury cathode, microgram quantities of copper, lead, cadmium, zinc, iron, cobalt, and nickel can be separated from at least 0.5M vanadium solutions. Quantitative recovery of all these traces of metals except cadmium from the mercury by distillation is satisfactory, and their subsequent estimation by either polarographic or spectrophotometric methods is adequate.

Electrolytic stripping of dilute amalgams at controlled potentials shows that the electrodeposited metals could not only be separated into the two major groups of passive (Fe, Co, and Ni) and nonpassive (Cu, Pb, Cd, and Cu) metals, but that separations within the nonpassive group are also possible.

INTRODUCTION

A mercury cathode has long been used to remove interfering metallic ions from solutions and to determine major constituents in mixtures of metals or metallic salts. However, it has only recently been used in conjunction with polarography to separate trace quantities of metals electrolytically before distillation of the Hg (1, 2).

In an effort to extend the electrolytic-polarographic method to the determination of trace metallic impurities in vanadium, some difficulties were encountered with regard to cadmium recovery after the distillation of mercury. Therefore, other methods of removing trace impurities were investigated.

Russell and co-workers (3, 4) determined the order of removal of 15 elements from amalgams by oxidizing agents and found that most common metals, except cobalt, nickel, and tungsten, could be removed without introducing large amounts of mercury ions. Liebhafsky (5, 6) reported that the oxidation rate of amalgams of copper, tin, thallium, lead, zinc, and cadmium by air in contact with acid, provided agitation is sufficiently violent, is virtually independent of the metal concentration and is limited mainly by the rate at which fresh amalgam is exposed. Therefore, since he concluded that the removal of these metals from mercury ought to become progressively easier as their concentration decreases, chemical oxidation might be used for nonselective recovery of metals deposited in a mercury cathode. It was shown (7) that treatment of dilute amalgams by various reagents either gave incomplete removal of the metal or introduced sufficient mercury salts to make subsequent determination of the trace amount of metal difficult.

Because chemical methods of removing trace metals from amalgams did not look too promising, a method involving electrolytic stripping was studied. Later the electrolytic-polarographic method (1) was adapted for stripping amalgams and for selective and successive removal of trace metals from a mercury cathode.

Since completion of this work, several studies of electrolytic decomposition of dilute amalgams have been published (8–10).

APPARATUS, MATERIALS, AND METHODS

Standard sulfate solutions of nickel, cadmium, zinc, and copper were prepared from C.P. or reagent grade shot or turnings. Since lead sulfate is insoluble, lead shot was converted to lead acetate. Cobalt solutions were prepared from reagent grade cobaltous sulfate. Iron solutions were prepared from primary standard ferrous ethylenediamine sulfate tetrahydrate or from reagent grade ferrous ammonium sulfate.

Pure solutions of vanadic sulfate or vanadyl sulfate were prepared from C.P. ammonium vanadate in two ways. A pure solution of vanadic sulfate was obtained directly by electrolysis of a suspension of ammonium vanadate in dilute sulfuric acid with a mercury cathode. Or, a hot acid solution of ammonium vanadate was converted stepwise by sulfur dioxide water to vanadyl sulfate, then by electrolysis to vanadic sulfate; excess sulfur dioxide was boiled off. Pure solutions of vanadyl sulfate were

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[2] Present address: Chemistry Department, George Washington University, Washington, D.C.

obtained by oxidizing pure solutions of vanadic sulfate with a stream of air or oxygen. Ordinarily the initial ammonium vanadate solutions contained 10 g vanadium per liter (0.2M) and sufficient sulfuric acid to supply hydrogen ions for conversion of ammonium vanadate to vanadic acid and for reduction of vanadic acid to vanadium(III). Reagent grade formic acid was added frequently to the vanadium solution to adjust the acidity; if the solution had already been purified by electrolysis, the formic acid was distilled before addition; otherwise, it was added without distillation.

Mercury was purified by oxidation with an Oxifier and filtration with a Gold-Adhesion Filter.[3] No significant amounts of metallic impurities were detected in this mercury.

The electrolysis cell has been described by Furman and co-workers (1). In some experiments an anode compartment, equipped with a fine sintered-glass disk, was mounted in the cell through a hole in the center of a Bakelite cover, and a tight fitting rubber crucible holder was used to adjust the depth of this compartment in the cell. If necessary, a cooling coil of 4 mm Pyrex tubing could be fitted beneath the anode compartment and connected to the faucet to cool the electrolyte. A suitable length of 15 gauge platinum wire alloyed with 10% iridium was used as the anode; a pool containing various amounts of mercury, usually 1.0–2.5 ml, served as the cathode. Power for the electrolysis was drawn through a rheostat from the laboratory d-c supply. A 12-in. split-tube furnace was employed for distillation.

The apparatus employed to regulate stripping was adapted from the diagram of a battery-operated electronic plating-cell control (11). Circuit changes to permit control of anodic potential instead of cathodic were made reversible. A more elaborate plating-cell control, which is a-c powered, could also be redesigned to permit stripping (12). Either circuit is entirely electronic in operation in contrast to those constant potential devices which utilize a number of mechanical parts. Simple all-electronic regulators pass the electrolysis current through vacuum tubes and thus possess limited current capacity. However, their current capacity is adequate for the stripping of dilute amalgams. References to other control devices have been listed elsewhere (13).

The stripping cell and its cover were made from the inner and outer parts of a 38/30 ground glass connection. The cell was 9 cm high and had a flat bottom which exposed the maximum stripping area of the mercury pool. The platinum-iridium contact to the pool just barely extended through the bottom. The cover was fitted with 7/25 ground glass joints in which a platinum cathode assembly and a probe from the salt bridge of a lead/lead sulfate reference electrode could be mounted. Probes varied in diameter from 4 mm to less than 1 mm; the tips were fitted with sintered-glass plugs. Both the stripping cell and the reference electrode were held by clamps having Tygon tubing on the prongs to maintain a high resistance pathway to ground.

A resistance not exceeding 20 megohms must be inserted between the reference electrode and the electrode under control. This resistance may be furnished by the internal resistance of an ordinary vacuum tube voltmeter, which is used to set the stripping voltage at the desired operating value. If the voltmeter has a high input impedance, its input leads should be shunted by a suitable resistance. A L&N vibrator type *p*H indicator[4] was used to measure all potentials, including *p*H.

Except for iron, which was estimated spectrophotometrically, metallic impurities were determined polarographically using a L&N Type E Electrochemograph. Both a Beckman Model DU and a Beckman Model B spectrophotometer were used for the spectrophotometric determination of iron.

Experimental

Electrolysis

In order to extend the electrolytic-polarographic method to the determination of trace impurities in vanadium, the separation of one metallic impurity from a vanadium solution was examined in the absence of all other metallic impurities except, of course, for the minute traces in the reagents. Since cadmium is not a usual impurity in most reagents, its recovery was studied first.

For these studies either 1.0 or 2.5 ml of purified mercury was introduced into the electrolysis cell followed by 100 ml of purified vanadium solution and an appropriate aliquot of the standard cadmium solution. The anode compartment, which was filled with 10 ml of 0.3*N* sulfuric acid, was lowered into the electrolyte through the Bakelite cover, and the depth was adjusted so that the anolyte level stood slightly above the catholyte level. The platinum-iridium anode was inserted to the bottom of the anode compartment, and a Gooch crucible was placed in the top of the compartment to prevent evaporation of the anolyte, which became quite hot during an electrolysis. Between 10 and 20 volts were applied to the cell, and the current was regulated to obtain the desired current density. At the end of the electrolysis, which was normally run overnight although some were run for shorter periods, the mercury cathode was removed from the cell and distilled, and the residue was analyzed polarographically.

The catholyte frequently acquired the purple color of vanadous ion within two or three hours. Usually the oxidation-reduction potential of the

[3] Bethlehem Apparatus Company.

[4] Catalogue No. 7664.

catholyte was measured at the completion of electrolysis, employing the mercury pool as the indicator electrode and a saturated calomel half-cell as the reference electrode.

In a series of 10 determinations of cadmium, ranging from 0.1 to 1 mg in weight, from 100 ml of 0.2M vanadium solution, the usual electrolytic-polarographic method gave recoveries of 39–93%. However, when lead or copper impurities were substituted for the cadmium, recovery of these metals was 95–103%. Since usually even traces of zinc could be determined quantitatively, it would appear that the potential of the vanadium redox buffer, which was obtained during the electrolysis, did not cause the low recoveries of cadmium. Thus, there seemed to be no need to obtain the most negative solution potential by separating anode and cathode compartments. When experiments were run without separating the anode from the cathode, recovery of impurities was equally good even though the vanadium solution did not acquire the dark purple color obtained when the electrodes were shielded from each other.

Many variables were considered in establishing optimum conditions for separating metal impurities at a mercury cathode, but most of them were found to have relatively minor or inconclusive effects on the recovery of lead, nickel, cadmium, and zinc. Current density, however, definitely improved reproducible recovery of zinc. Table I shows that a current density of not less than 0.45 amp/cm² should be used for consistent quantitative recoveries. Changes in current densities given in Table I were accomplished by increasing the current passing through the electrolysis cell and/or by decreasing the volume, and therefore area, of the mercury cathode.

Electrolyses of identical solutions were carried out for varying lengths of time, and the results of these experiments are shown in Table II.

Results of Tables I and II indicate that recovery of cadmium is about 5–10% below recovery of lead, nickel, and zinc. The poor recovery of cadmium was shown subsequently to be a result of the volatility of this element during distillation.

The conditions of electrolysis which were established for achieving essentially complete recoveries of the metallic impurities from vanadium were: volume of mercury, 1.0 ml; current strength 0.8–1.0 amp; current density, 0.45–0.9 amp/cm²; volume of electrolyte, 100 ml; maximum concentration of vanadium, 0.2M; separation of anolyte and catholyte, unnecessary; acids, sulfuric only, with no anode compartment; length of electrolysis, as short as 6 hr.

Distillation and Polarographic Analysis

After electrolysis the dilute amalgam electrode was drained into a silica boat without interrupting the current. The last drop of amalgam was received on a dry filter paper to prevent contamination by a trace of electrolyte, then added to the boat. Usually a small globule of mercury still remained in the cell following this procedure. This was removed by running out a small amount of the electrolyte into a filter paper cone with the stopcock turned completely open for a brief moment; it was blotted dry and added to the boat. If a small amount of vanadium solution contaminated the amalgam during its removal, the nickel and zinc polarographic waves were obscured and quantitative measurements were impossible.

The boat temperature was observed during the distillation with a thermometer inserted through the cork stopper at the inlet of the combustion tube. The tube was swept by a stream of tank nitrogen, and the mercury vapor was condensed in a beaker of water. The temperature was elevated quickly and maintained at 350°–360°C until only the metal impurities remained. Generally, the power was cut off as soon as the last of the mercury had volatilized. When the boat returned nearly to room temperature, it was removed through a cylinder of paper, which prevented droplets of condensed mercury from adhering to the walls of the boat.

The boat was placed in a silica beaker and the residue was dissolved with 3 ml of aqua regia. After the boat was rinsed by a small stream of distilled water and removed from the beaker, the solution was evaporated to dryness. The residue was dissolved in 0.5 ml of hydrochloric acid plus an aliquot

TABLE I. *Recoveries of zinc and other metals from 100 ml of approximately 0.2M vanadium solution*

Current density amp/cm²	Pb	Metal found, Ni	% Cd	Zn
0.03–0.06	—	—	—	24*
0.06–0.12	—	—	—	65*
0.20–0.25	95	87	—	100
0.20–0.25	105	97	—	96
0.10–0.15	83	89	75	95
0.10–0.15	87	92	77	81
0.45–0.9	99	96	84	97
0.45–0.9	100	95	92	96
0.45–0.9	101	95	81	96

* 0.5 mg of metal added; all other additions were 0.1 mg. All electrolyses proceeded for a minimum of 11 hr.

TABLE II. *Recoveries from 100 ml of 0.2M vanadium solution by electrolysis at a current density of 0.6–0.9 amp/cm²*

Electrolysis period, hr	Pb	Metal taken, mg			Metal found, %			
		Ni	Cd	Zn	Pb	Ni	Cd	Zn
1	0.101	0.096	0.102	0.101	41	10	49	28
3	0.101	0.096	0.102	0.101	71	30	57	31
6	0.101	0.096	0.102	0.101	104	96	87	105
9	0.101	0.096	0.102	0.101	102	93	91	96

TABLE III. *Typical recoveries of cadmium from an amalgam by distillation*

Volume of Hg, ml	Cd taken mg	Cd found mg	Cd found %
In a stream of nitrogen			
2.5	0.083*	0.080	96
2.5	0.092*	0.084	91
2.5	0.096*	0.089	93
2.5	0.101	0.091	90
2.5	0.479	0.390	82
1.0	1.243	1.056	85
In a stream of air			
1.0	0.0215	0.0215	100
1.0	0.0917	0.0879	96
1.0	0.1226	0.1192	97

* Lead, nickel, and zinc also present (0.1 mg of each).

of solution containing 25 mg of potassium chloride and the evaporation was repeated. Following addition of another 0.5 ml of hydrochloric acid together with a little water, the residue was evaporated a third time. Heating was stopped while the odor of hydrogen chloride was faint in the dry residue. The final residue was dissolved in 2.90 ml of water, to which was usually added a drop (0.05 ml) of 0.2% methyl cellulose as maximum suppressor. The solution was placed in a polarographic cell, deaerated for 5–10 min by a stream of tank nitrogen, then polarographed. Lead and cadmium were determined from their diffusion currents in this medium. The polarographic waves of copper, nickel, and zinc, as well as cadmium, are well separated in an alkaline background, and were determined in a pyridine-pyridinium chloride medium or in an ammonia-ammonium chloride medium. Since pyridine-pyridinium chloride is preferable when iron is present (14), this medium was used almost exclusively for the alkaline background. After the polarogram was recorded from acid solution, one drop of hydrochloric acid and five drops of pyridine (0.15 ml) were added to the polarographic solution. Ordinarily no difficulty was encountered in obtaining typical waves for each metal, although in a number of samples the zinc and pyridine waves were partially coalesced.

A strictly comparative polarographic method was employed. Using the same capillary and the same experimental conditions, heights of the characteristic waves obtained from unknown solutions were usually compared with heights obtained from identical, or nearly identical, standard solutions. Interpolation between the values for two different known concentrations was occasionally used to obtain a value for a third concentration.

With the optimum electrolysis conditions the recoveries of cadmium that could be expected from an amalgam by the distillation and polarographic method are shown in Table III. Since nearly all the recoveries of cadmium reported by Furman and co-workers (1) lie in the 95–100% range, some loss of cadmium by volatilization was suspected as being the most likely source of this discrepancy. This may be prevented by selective oxidation of cadmium vapors in the presence of mercury vapors. Several distillations of cadmium amalgams were made with an air stream passing slowly through the distillation tube. Although some mercury was oxidized, this did not interfere with polarographic analysis of the cadmium residues (Table III). As a further proof that cadmium was volatilized when a stream of pure nitrogen was used during the distillation operation, both the mercury distillate and the walls of the distillation tube were found to contain about 3% of a cadmium sample.

Electrolytic Stripping

Deposition of metallic ions at controlled potentials has long been used as a method to separate metals selectively. Recently the development of adequate instruments to control the cathode potential automatically has stimulated renewed interest in this method (15, 16). The reverse process, selective stripping of metals from an electrode into a solution at a controlled anode potential, has not been similarly exploited for analytical separations. However, Kozlovskii and co-workers (17) have recently reported amalgam methods of separation for macro quantities of nonferrous metals which utilize controlled anodic oxidation. Moreover, anodic dissolution has been used for many years to dissolve solid alloy samples, to measure the thickness of plated coatings, and to determine nonmetallic inclusions in metals (15).

If the anodic oxidation of metals from amalgams follows the same pattern as that reported (3, 4) for oxidizing solutions, base metals should strip very readily from amalgams at controlled potentials, whereas the removal of iron, cobalt, and nickel from amalgams without introduction of mercury ions may not be possible. Thus in composite amalgams, i.e., in amalgams containing several metals, it should be possible to separate zinc, cadmium, lead, and copper from iron, cobalt, and nickel even though the effect of large concentrations of the passive metals on the stripping of the nonpassive metals may introduce some unexpected difficulties.

The degree of separation attainable by electrolytic stripping of amalgams should be determined by the minimum concentration of metal required to maintain the potential of an amalgam. Erdey-Gruz (18) and others (19–22) showed that for amalgams with a concentration of 10^{-5}–10^{-4} g-atom/l, the potential

is determined solely by the electrochemical distribution: equilibrium metal/metallic ion. Thus, the concentration effect follows the Nernst equation. In the concentration range 10^{-6}–10^{-5} g-atom/l, the change of potential is greater than that demanded by the Nernst equation. If the concentration of the amalgam falls below 10^{-6} g-atom/l, the potential is the same as that of pure mercury. From these data the number of micrograms of a given metal which remain in a 1.0 ml amalgam electrode when the potential of the electrode is the same as that of pure mercury may be calculated. Results are: zinc, 0.06; cadmium, 0.1; lead, 0.2; and copper, 0.06 μg. If the mercury electrode contained initially 10 μg of each of these metals, the following percentages of metals would remain in the mercury after stripping: zinc, 0.6%; cadmium, 1%; lead, 2%; and copper, 0.6%. Thus, for samples containing about 10 or more μg of a given metal, the unstripped fraction should be no larger than the uncertainty of the subsequent polarographic analysis.

Stripping of nonpassive metals.—The recovery of trace metals from an amalgam by electrolytic stripping was applied to many amalgams containing various amounts of one or more of the metals, copper, lead, cadmium, and zinc. Amalgams were prepared by electrolyzing known amounts of these metals in solutions from a 0.1*N* sulfuric acid or dilute acetic acid solution into a known weight of mercury. If the amalgam was not prepared directly in the stripping cell, it was drained into this cell in the manner described above. Otherwise, at the completion of electrolysis the electrolyte was siphoned without interrupting the current, and the vessel was rinsed with water until the conductance of the solution was negligible.

The stripping electrolyte generally consisted of 5 or 10 ml of 0.1–0.5*N* potassium sulfate or potassium chloride. Potassium sulfate was preferred, especially for stripping copper amalgams, because of the greater potential difference between mercury-mercurous sulfate and the amalgam as opposed to the potential difference between mercury-mercurous chloride and the amalgam. However, it was essential to use potassium chloride when the amalgam contained lead. Obviously, the number of metals which can be separated from mercury by the stripping process and the degree of selectivity of the separations among the metallic impurities will vary with the composition of the stripping electrolyte.

Copper amalgams, which formed a coating of cuprous oxide on the surface of the amalgam in a neutral electrolyte, were slightly acidified with a drop of acetic acid. If the electrolyte was initially neutral, it became basic during the stripping. Hydroxides of zinc, cadmium, and lead, which formed a readily visible precipitate when the amalgam contained about 1 mg or more of one of these metals, did not appear to interfere in any way with the stripping process. Ordinarily the solution did not become sufficiently basic to establish the potential of the mercury-mercuric oxide couple, which is considerably more negative than the potentials of the mercury-mercurous salt couples.

A quiescent mercury pool strips fairly rapidly and smoothly. For example, the current-time data for the stripping of 124 μg of cadmium from 5 and 15 g of amalgam are shown in Fig. 1, where the maximum stripping rate was used. This rate was attained by setting the electronic control so that the stripping would stop at a potential 0.5–0.1 v before the dissolution of mercury would begin. As can be seen from Fig. 1, the initial current during a stripping operation was almost a "surge current" but rapidly fell during the first minute to a value of several hundred microamperes. The stripping operation was considered to be complete when the current fell to about 0.1 μa. The current was never observed to reach a zero value unless extremely long times were allowed for the amalgam to reach equilibrium.

Although rotating the amalgam or stirring the solution increased the rate of stripping, neither of these stirring procedures was employed. Passing oxygen or nitrogen through the solution appeared to have no effect other than that of stirring. This has

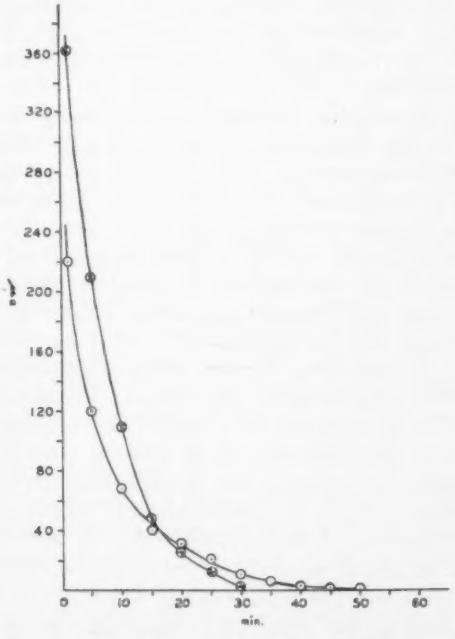

FIG. 1. Current-time curves for discharging dilute amalgams. ⊗ = 5g; ⊙ = 15g.

TABLE IV. *Typical recoveries from simple and composite amalgams by the stripping procedure*

Wt of Hg, g	Metal taken, mg				Metal found, %			
	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn
5.0	0.0101	—	—	—	95	—	—	—
34.0	0.0101	—	—	—	98	—	—	—
5.0	0.0248	—	—	—	99	—	—	—
5.6	0.1223	—	—	—	98	—	—	—
15.0	1.216	—	—	—	99	—	—	—
5.0	1.243	—	—	—	98	—	—	—
28.0	2.486	—	—	—	97	—	—	—
28.0	6.215	—	—	—	100	—	—	—
20.2	—	1.012	—	—	—	100	—	—
34.0	—	—	0.498	—	—	—	98	—
34.0	—	—	0.498	—	—	—	100	—
34.0	—	—	—	0.458	—	—	—	97
34.0	1.243	—	0.498	—	100	—	104	—
5.0	0.124	—	—	0.498	101	—	—	102
34.0	0.124	—	—	0.498	103	—	—	95
34.0	0.124	—	0.498	0.498	103	—	101	102

been reported previously by Bowden (23) and indirectly by Liebhafsky (5, 6).

In a number of cases dilute amalgams containing about 50 μg or less of zinc or cadmium in 1–2.5 ml of mercury did not give an amalgam potential when prepared for stripping. This behavior, which was more common with zinc amalgams than with cadmium amalgams, was traced to the spontaneous decomposition of the dilute amalgams. For example, an amalgam composed of 13.5 g (1 ml) of mercury and 44 μg of zinc, which was allowed to stand for 20 min in contact with 5.00 ml of ammonia-ammonium chloride solution, was completely decomposed as shown by the polarographic determination of zinc in the solution.

If desired, the amalgam potential could be regained by electrolyzing the stripping electrolyte with the mercury pool as the cathode for a minute or two at 0.1–0.2 amp. If potassium was deposited, it began to react with the solution as soon as the electrolysis current was broken. Thus, when the cell was prepared for stripping, the potential of potassium amalgam was obtained and persisted until all the potassium had reacted. The potential of zinc or cadmium amalgam was now obtained and the stripping could be followed in the usual manner. It was shown that zinc or cadmium ions could be removed quantitatively from solution by an internal electrolysis utilizing the reaction of a potassium amalgam alone on the solution to deposit the less active metals.

Solutions from the stripping operation were analyzed in one of two ways. If the stripping was performed in a known volume of electrolyte, the resulting solution was merely polarographed. Otherwise, the stripping solution was acidified with acetic acid, then evaporated to dryness. The residue was dissolved in a known volume of water or neutral electrolyte (potassium sulfate or potassium chloride) and polarographed as described previously.

Typical recoveries of metals from simple and composite amalgams are shown in Table IV, and clearly indicate that quantitative results were obtained in all cases.

Use of an internal electrolysis instead of electronically controlled electrolytic stripping to recover nonpassive metals from a mercury electrode was tested by discharging an amalgam containing nonpassive cadmium and passive nickel against a half-cell composed of a copper amalgam electrode and a solution of saturated copper sulfate slightly acidified with sulfuric acid. Each amalgam pool, together with its appropriate electrolyte, was contained in an open stripping cell which was connected to the opposing cell by a salt bridge of agar and saturated potassium sulfate. A resistor was included in the discharging circuit to limit the initial current to about 100 μa or less. Eventually, as the potential difference between the half-cells decreased, this external resistance was removed, and the half-cells were short-circuited until the current became negligible. A saturated calomel reference electrode was included to check the potential of both amalgam electrodes.

Recoveries of cadmium from amalgams containing cadmium and nickel using the internal electrolysis technique for cadmium removal were determined polarographically and averaged 101 ± 1%. The amalgam remaining after the removal of cadmium was distilled, and nickel recovery was 99 ± 2%. Therefore, the very simple internal electrolysis assembly can be used to separate passive from nonpassive metals from an amalgam without introducing mercuric ions into solution.

Stripping of passive metals.—Separation of cadmium from nickel by means of internal stripping and the work of Russell (3, 4) suggested that the passive metals, iron, cobalt, and nickel, would be removed from mercury, if at all, only after copper was removed. When the stripping of amalgams of nickel and iron was attempted, no detectable amount of either element could be found in the electrolyte unless mercury was also dissolved. However, small to substantial amounts of cobalt were stripped in a sulfate electrolyte at a potential close to the dissolution potential of mercury, but complete removal of the cobalt was never attained without resorting finally to distillation. In no case where stripping was performed so that no mercuric ions were introduced into solution was any trace of the nonpassive metals detected in the distillation residue.

Typical recoveries from a mercury electrode by stripping of one or more nonpassive metals in the presence of one or more passive metals, together with the recoveries of the passive metals by the dis-

TABLE V. *Typical recoveries of nonpassive metals from a mercury electrode by the stripping procedure and of passive metals by the distillation procedure*

Wt of Hg g	Nonpassive metal taken, μg				Passive metal taken, μg			Nonpassive metal found, %				Passive metal found, %		
	Cu	Pb	Cd	Zn	Fe	Co	Ni	Cu	Pb	Cd	Zn	Fe	Co	Ni
20.2	1012	—	—	—	—	—	56	97	—	—	—	—	—	97
5.0	1012	—	—	—	—	500	—	103	—	—	—	—	103	—
13.5	—	500	—	—	500	—	—	—	98	—	—	*	—	—
13.5	—	—	—	456	—	500	—	—	—	—	100	—	104	—
13.5	—	—	17	—	—	—	56	—	—	101	—	—	—	100
34.0	—	—	25	—	0.1g	—	—	—	—	103	—	*	—	—
13.5	—	—	110	—	—	—	56	—	—	102	—	—	—	101
13.5	—	—	110	—	—	—	565	—	—	100	—	—	—	97
20.2	—	—	110	—	—	—	565	—	—	103	—	—	—	*
20.2	—	—	125	—	—	—	565	—	—	98	—	—	—	100
34.0	—	—	125	—	500	—	—	—	—	101	—	105	—	—
5.0	—	—	1251	—	—	—	56	—	—	96	—	—	—	97
5.0	1012	—	876	—	—	500	—	103	—	98	—	—	103	—
20.2	—	—	876	—	—	500	565	—	—	99	—	—	102	96
5.0	—	1000	876	450	—	500	565	—	102	100	99	—	105	95
5.0	—	—	—	—	1000	—	—	—	—	—	—	100	—	—
13.5	—	—	—	—	—	—	56	—	—	—	—	—	—	96
13.5	—	—	—	—	—	500	565	—	—	—	—	—	105**	97
13.5	1012	—	—	—	—	500	—	99	—	—	—	—	105†	—
20.2	—	—	112	—	—	500	—	—	—	100	—	—	53‡	—

* Per cent found was not determined.
** 16% cobalt was found in stripping step.
† 7% cobalt was found in stripping step.
‡ 53% cobalt was found in stripping step; distillation was omitted.
Stripping of the passive metals was attempted in the bottom five samples.

TABLE VI. *Typical recoveries from 0.2M vanadium solution using the stripping and distillation procedures*

Wt of Hg g	Metal added μg						Metal found (stripping) %			Metal found (distillation) %		
	Cu	Pb	Cd	Fe	Co	Ni	Cu	Pb	Cd	Fe	Co	Ni
13.5	—	—	25	—	—	—	—	—	97	—	—	—
13.5	—	—	50	—	—	—	—	—	98	—	—	—
13.5	—	—	124	—	—	—	—	—	98	—	—	—
13.5	—	—	124	—	—	—	—	—	101	—	—	—
13.5	—	—	1243	—	—	—	—	—	98*	—	—	—
28.0	—	—	2486	—	—	—	—	—	97	—	—	—
20.2	—	—	876	10mg	—	—	—	—	96	†	—	—
20.2	—	—	876	—	500	565	—	—	99	—	102	96
13.5	—	—	1251	—	500	565	—	—	98	—	100	95
13.5	—	500	876	—	500	565	—	103	103	—	102	97
13.5	1012	—	876	500	500	565	99	—	97	†	96	100
20.2	2024	500	250	500	500	565	100‡	98	101	†	104	97

* The electrolyte was 0.5M in vanadium.
† Not determined.
‡ Separated by distillation instead of stripping.

tillation of the mercury, are shown in Table V. Iron was determined spectrophotometrically by the *o*-phenanthroline method (24). Special attention should be called to the sample in which 25 μg of cadmium were recovered from 34.0 g of mercury containing 0.1 g of iron. Presumably, deposition followed by stripping could be used as a general method for separating a small amount of a nonpassive metal from a large amount of a passive metal.

Application to vanadium salts.—Using the optimum conditions for electrolysis of vanadium solutions, as given previously, the electrodeposited "impurities" were recovered and analyzed according to the procedures just given. The results of typical recoveries of trace amounts of six metals from 100 ml of 0.2M vanadium solution using this procedure are shown in Table VI. It is significant that all metals listed in Table VI (cf. Tables I and II) are obviously separated from vanadium by electrolysis and subsequently recovered from mercury by the procedure employed.

Discussion

The accuracy of the polarographic analysis of a mixture depends on the ratio in which the various substances occur. The determination of a cation in a solution containing a group of metal ions for which the half-wave potentials differ by about 0.2 v or more is readily accomplished if the cations are present in similar concentrations in the range 10^{-3}–10^{-5}M. When the cations are present in concentrations which vary widely, the determination is still readily accomplished if the concentration of each cation *increases* in the order of decreasing reducibility. If, however, the concentration of each ion *decreases* in the order of decreasing reducibility, the accuracy of the analysis progressively drops as the difference in the concentrations of the cations becomes greater. Thus separation of the nonpassive and passive metals by stripping and distillation procedures described here,

together with selective stripping among nonpassive metals, greatly simplifies polarographic analysis of a mixture of metals which has been electrodeposited with a mercury cathode.

Presumably, the nonpassive metals could be analyzed coulometrically while being selectively stripped at a controlled potential, unless there were sufficient spontaneous decomposition of the amalgam to invalidate the measurements. Either the quantity of electricity or the discharging time, which was recently studied by Juliard and Gierst (25), could be measured. The latter measurement is dependent on the weight and dimensions of the liquid pool.

An estimate of the agreement between the quantity of electricity put through a stripping cell by the control apparatus and the amount of metal stripped was made by stripping a 1.24 mg sample of cadmium while the cell current was held constant within 10% by manual control of the constant potential device. For example, the current was held initially to 500 ± 50 μa for over 56 min, then it was held to 50 ± 5 μa, etc., until completion of the process. This crude technique accounted for 1.7 coulombs of the theoretical 2.1 coulombs required to strip 1.24 mg of cadmium, if no spontaneous reaction of the metal with the electrolyte occurred.

The results in Fig. 1 show clearly that the initial current in the smaller pool (area, approximately 1.3 cm^2) was considerably greater than the initial current in the larger pool (area, approximately 3.5 cm^2). Moreover, the smaller pool, having the smaller surface area, discharged at a faster rate, and eventually the two curves crossed. Thus, in a cadmium amalgam the cadmium must be distributed throughout the mercury rather than concentrated near the amalgam-electrolyte interface. Otherwise, the larger pool, having the larger surface area, would have discharged more rapidly. This conclusion regarding the homogeneity of cadmium amalgams should be checked for the various metal amalgams because the same results may not be obtained with all metals.

Summary

By electrolysis, copper, lead, cadmium, and zinc present in quantities as small as 10 μg, may be removed essentially quantitatively from solutions as concentrated as 0.5M in vanadium. The small quantities of nonpassive metals (copper, lead, cadmium, and zinc) may then be recovered by back electrolysis at controlled potentials, and the passive metals (iron, cobalt, and nickel) may be recovered by the distillation of the mercury cathode following this stripping. All the metals may be recovered by distillation, but losses of cadmium are likely to occur unless the nitrogen stream is mixed with a sufficient amount of oxygen or air. Subsequent estimation of the metals may be made polarographically or by any other valid method. Use of the stripping technique to separate the electrodeposited metals into two groups, as well as the possibility of selective and successive stripping within the nonpassive group, simplifies the polarographic analysis.

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Magnesium Fluorosilicate Phosphors[1]

P. W. Ranby and S. T. Henderson

Thorn Electrical Industries, Ltd., London, England

ABSTRACT

The preparation of phosphors with a matrix of magnesium, silicon, oxygen, and fluorine, and activated by titanium or titanium and manganese is described. X-ray data are given. The materials when excited by mercury resonance radiation have wide emission bands with a high proportion in the long wave-length region of the spectrum. They are useful fluorescent lamp phosphors. The mechanism of luminescence appears to be sensitization by titanium, although there are unusual features in the case.

Introduction

This paper describes a new phosphor which can be used in fluorescent lamps. It is a magnesium fluorosilicate activated by titanium; incorporation of manganese produces a change in the color of the emission so that a range of materials with fluorescence varying from greenish-yellow to orange-pink can be obtained. An outstanding feature of these materials, whether manganese is present or not, is the high proportion of red in the fluorescent emission. This fact, combined with their good maintenance characteristics, makes them of special interest in the manufacture of fluorescent lamps of good color rendering properties. Another advantage is that these phosphors are prepared from relatively inexpensive and plentiful raw materials and require no elaborate atmosphere control during their preparation.

Magnesium meta- and ortho-silicates activated by titanium have been known as luminescent materials for some time and a few of their properties have been briefly described (1). The proportion of titanium used in order to obtain maximum luminescence is high, e.g., 10 molar % of the matrix, and the color of the luminescence is blue. Manganese cannot be incorporated in these silicates as an additional activator, but magnesium silicate containing manganese alone is known to emit a red luminescence under cathode rays. Recently, Anderson and Wells (2) have described a wide range of magnesium silicates and titanosilicates prepared in the presence of magnesium fluoride; they fluoresce greenish-yellow when excited by short wave ultraviolet radiation. These latter materials resemble the previously known titanium-activated magnesium silicates in that the preferred concentration of titanium in the matrix is high, but differ in that if manganese is incorporated in addition to the titanium, then the color of the luminescence excited by cathode rays is moved toward the red.

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For maximum brightness, the magnesium fluorosilicate phosphors described below (3) require a high proportion of magnesium fluoride, but only a low concentration of titanium dioxide during their preparation; also, the incorporation of manganese markedly alters the color of the luminescence excited by short ultraviolet radiation, and the materials therefore differ from those described by Anderson and Wells.

Nature of Matrix

The term "fluosilicate" is normally used to describe a salt of fluosilicic acid H_2SiF_6, and consequently an acid radical free from oxygen. In the present paper the term magnesium fluorosilicate is used to indicate a matrix in which silicon, oxygen, and fluorine are all combined together with magnesium.

If a mixture of magnesium oxide and silica in the metasilicate proportions is heated at about 1100°C with 2 moles of magnesium fluoride per mole of silica a product is obtained which x-ray analysis shows to be a new phase. X-ray diffraction lines for such a magnesium fluorosilicate are shown in column 1 of Table I. Columns 2, 3, and 4 list the characteristic x-ray diffraction lines of magnesium ortho- and meta-silicates and magnesium fluoride, respectively, as given by Hanawalt, Rinn, and Frevel (4), and column 5 the lines for norbergite from the A.S.T.M. index.

Materials having the structure of this magnesium fluorosilicate provide the matrix for the new phosphors. The x-ray pattern of a fluorosilicate containing titanium and manganese is virtually indistinguishable from that of the unactivated matrix. This shows considerable agreement with the pattern of norbergite apart from lines in the latter which appear to be due to magnesium orthosilicate. On the other hand, x-ray examination of materials prepared according to the examples given by Anderson and

TABLE I. *X-ray powder diffraction lines of magnesium fluorosilicate, orthosilicate, metasilicate, and fluoride, and norbergite,* $Mg_2SiO_4 \cdot (F,OH)_2$

Magnesium fluorosilicate		Magnesium orthosilicate		Magnesium metasilicate		Magnesium fluoride		Norbergite	
d	Intensity	*d*	Intensity	*d*	Intensity	*d*	Intensity	*d*	Intensity
5.10	medium	5.10	0.11	3.16	1.00	3.29	0.80	5.2	0.4
4.33	medium	3.89	0.40	2.91	0.33	3.14	0.05	4.8	0.4
4.07	medium	3.72	0.05	2.72	0.20	2.56	0.20	4.41	0.5
3.33	weak	3.49	0.20	2.55	0.27	2.24	1.00	3.37	0.6
3.22	weak	2.99	0.13	2.30	0.20	2.07	0.32	3.08	0.8
3.05	very strong	2.77	0.40	1.97	0.47	1.93	0.12	2.94	0.4
2.64	strong	2.51	0.32	1.71	0.10	1.72	1.00	2.77	0.4
2.46	weak	2.45	0.40	1.64	0.13	1.64	0.32	2.66	0.7
2.40	medium	2.26	0.40	1.490	0.40	1.53	0.20	2.52	0.6
2.34	medium	2.15	0.11	1.312	0.27	1.460	0.05	2.43	0.4
2.29	weak	2.02	0.02			1.437	0.01	2.35	0.4
2.26	medium	1.95	0.02			1.408	0.01	2.26	0.8
2.23	strong	1.88	0.03			1.378	0.60	2.03	0.2
2.03	very weak	1.81	0.03			1.340	0.01	1.94	0.6
1.94	weak	1.74	1.00			1.319	0.08	1.86	0.2
1.84	weak	1.67	0.10					1.81	0.2
1.73	strong	1.62	0.11					1.74	1.0
1.70	very weak	1.57	0.08					1.65	0.5
1.612	weak	1.490	0.32					1.60	
1.597	weak	1.395	0.20					1.54	0.2
1.578	weak	1.350	0.28					1.49	0.8
1.524	weak	1.315	0.10					1.47	0.4
1.476	medium							1.41	0.4
1.454	medium							1.35	0.6
1.401	very weak								
1.331	weak								

In all columns *d* represents the interplanar spacing in Ångström units. The terms in column 1 correspond approximately to the intensity values, as follows: very strong = 1.0–0.80; strong = 0.80–0.60; medium = 0.60–0.40; weak = 0.40–0.20; very weak = below 0.20.

Wells (2) shows that they have a crystal structure which is very similar to magnesium orthosilicate.

Preparation of Phosphors

A convenient method of preparation of the phosphor is to heat an intimate mixture of 1 mole magnesium oxide and 1 mole silica with 2 moles magnesium fluoride and about 0.015 mole titanium dioxide, but alternative starting materials can be used, such as ammonium fluoride with additional magnesium oxide in place of the magnesium fluoride in the initial mixture. Heating is carried out at 1100°–1200°C in air and, despite the high concentration of fluoride in the mixture, ordinary silica crucibles do not show excessive attack during the heating and can be used satisfactorily in the preparation. Some fluorine and silicon are lost during the firing, hence the value of the x-ray pattern for identification of the phosphors. Fairly wide variations in the ratios of the matrix-forming components can be used and these produce relatively small differences in the intensity of the fluorescence of the product.

When manganese is incorporated in addition to titanium it may be added to the mixture before firing in the usual way as carbonate, nitrate, fluoride, etc.

General Luminescence Characteristics

When excited by short wave-length ultraviolet, e.g., 2537 Å radiation, these phosphors emit a bright greenish-yellow fluorescence if activated by titanium alone. If manganese is present as well, the color of the fluorescence changes through yellow to pink with increasing concentration of manganese. Fig. 1 shows a selection of spectral energy distribution curves. The intensity of luminescence decreases only slowly with rise in temperature of the phosphor above room temperature, as shown in Fig. 2 for phosphors with and without manganese. Materials free from manganese are practically nonfluorescent under long wave-length ultraviolet, e.g., 3650 Å radiation, but they

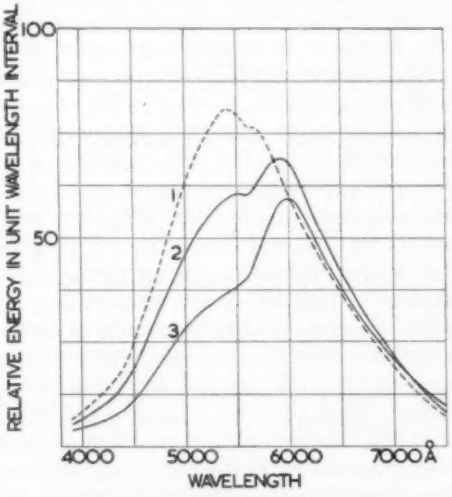

FIG. 1. Spectral energy distribution curves of fluorosilicate phosphors under 2537 Å, plotted on a wave-length basis. Curves 1–3 refer to phosphors with 0, 0.1, 0.2% Mn by weight, respectively.

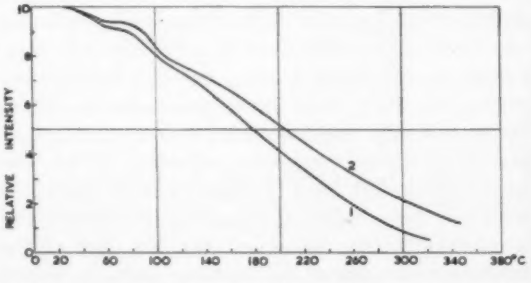

FIG. 2. Effect of temperature on fluorescent intensity under 2537 Å, measured through viscor filter. Curves normalized to 20°C. Curve 1, phosphor with Ti only; curve 2, phosphor with Ti and Mn.

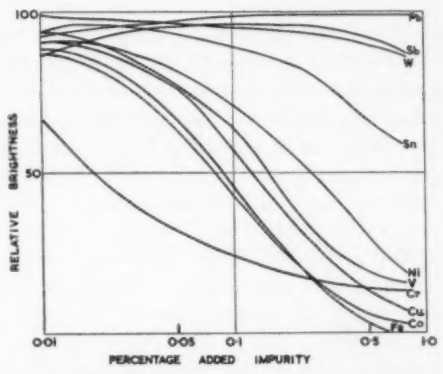

FIG. 3. Reduction of fluorosilicate brightness under 2537 Å by traces of impurities. Phosphor contains Ti but no Mn. Impurities in per cent by weight.

show a weak yellow-pink fluorescence if manganese is incorporated. The main region of the excitation spectrum of the material overlaps the low pressure mercury resonance line at 2537 Å (5).

The intensity of the fluorescence is greatly reduced by the presence of traces of certain impurities incorporated in the matrix during preparation. Especially harmful are traces of the transition elements which occur in the same periodic series as titanium and manganese, whereas much higher concentrations by weight of lead, antimony, tungsten, and to a slightly lesser extent tin, can be tolerated (see Fig. 3). The transition elements, though normally having colored ions in solution, do not appear to be causing loss of efficiency merely by discoloration of the phosphor matrix: for example, as much as 0.5% copper can be incorporated with only slight discoloration.

USE OF MAGNESIUM FLUOROSILICATE PHOSPHORS IN LAMPS

Fluorescent lamps using the titanium-activated magnesium fluorosilicate give an initial efficiency of 58 lpw for the 48 T12 40W type, with indications that this will be improved after further experience. The very good lumen maintenance (e.g., 95% at 100 hr, 92% at 500 hr) is characteristic of the phosphor. Lower brightnesses are obtained from lamps made with materials containing manganese. Fig. 4 shows the chromaticity on the C.I.E. color triangle of 48T12 40W lamps made from phosphors containing increasing concentrations of manganese. Incorporation of manganese produces a drift in color across the black body locus but, owing to the mechanism by which the color change is produced, the initial efficiency of a lamp giving a color close to the black body line is only 39 lpw.

Since the material activated by titanium without manganese emits strongly in the red, this phosphor is of particular interest for incorporating in blends

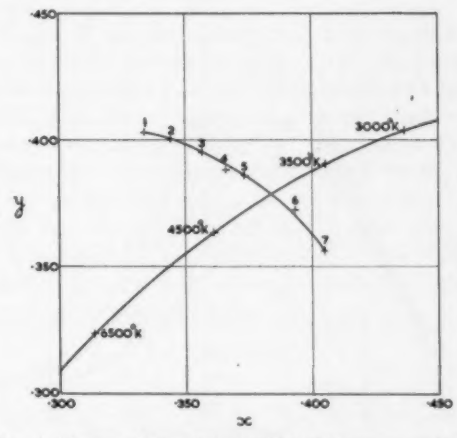

FIG. 4. Chromaticity plot of 48T12 40W lamps containing fluorosilicate phosphors. Phosphors 1–7 contain 0, 0.05, 0.14, 0.24, 0.28, 0.48, 0.75% Mn by weight, respectively.

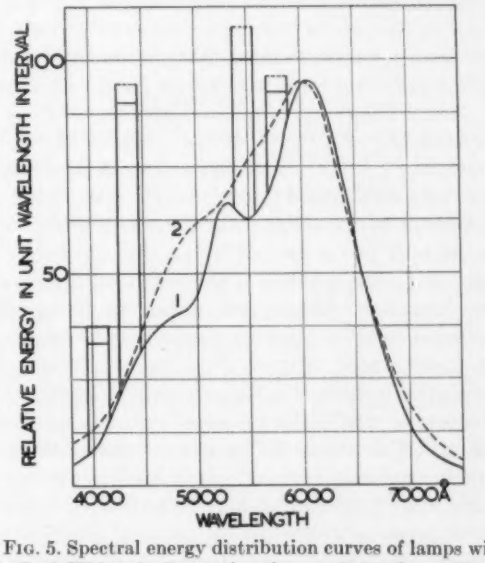

FIG. 5. Spectral energy distribution curves of lamps with (1) Cool White de Luxe phosphor and (2) fluorosilicate 4500°K blend.

with other phosphors of good maintenance in order to obtain fluorescent lamps with improved color rendering properties. A lamp of 4500°K color with good red emission is thus obtained from a mixture of approximately 50 parts magnesium fluorosilicate (Ti), 25 parts calcium silicate (Pb, Mn), and 25 parts barium titanium phosphate; the spectral energy distribution is shown in Fig. 5, compared with a conventional Cool White de Luxe lamp. Lamps using the fluorosilicate 4500° K blend have initial efficiencies of 51 lpw with good maintenance characteristics.

SPECTRAL ENERGY DISTRIBUTION OF FLUORESCENCE

Spectral energy distribution measurements on phosphors containing titanium but spectrochemically

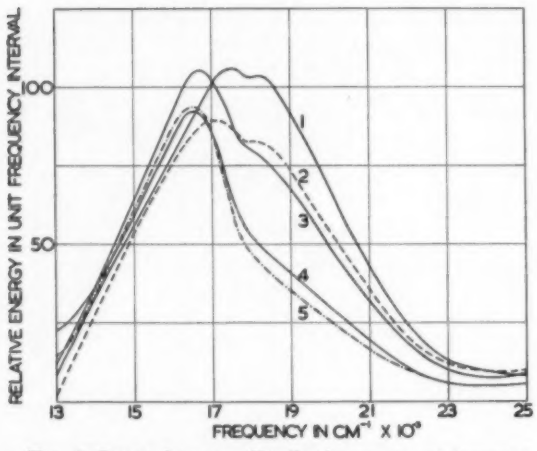

FIG. 6. Spectral energy distribution curves of fluorosilicate phosphors under 2537 Å, plotted on a frequency basis. Curves 1–5 refer to phosphors with 0, 0.05, 0.1, 0.2, 0.3% Mn by weight, respectively.

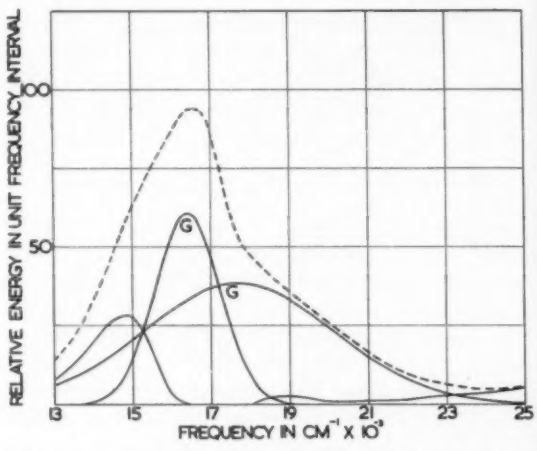

FIG. 7. Analysis into Gaussian bands (GG) of spectral energy distribution curve of fluorosilicate phosphor containing 0.3% Mn (as curve 5, Fig. 6).

free from manganese show that the emission under 2537 Å radiation consists of a wide band with a peak at about 17700 cm^{-1} and a distribution close to Gaussian (curve 1, Fig. 6), with $a = 8.45 \times 10^{-8} cm^2$ in $I = I_o \exp \{-a (\nu - \nu_o)^2\}$. An unusual feature which has been established by repeated trials, both on fluorescent lamps made with the phosphor and also on the bulk power excited by an external source of radiation, is the splitting of the peak into two closely spaced maxima. These peaks appear to diverge and become distinct as increasing amounts of manganese are incorporated (curves 2–5, Fig. 6). When the manganese content is sufficient, analysis of the band structure is possible by the usual methods, as shown in Fig. 7. This shows the presence of the 17700 cm^{-1} band in moderate amount, and at least two bands of longer wave length which may be attributed to manganese presumably excited by a normal sensitization process. The separation of these bands, 1600 cm^{-1}, is similar to that found for manganese bands in the halophosphates (6) and pyrophosphates (7). The main band attributed to manganese is at 16400 cm^{-1}, and it seems likely that this will move to somewhat higher frequency when the manganese content decreases. This position is so close to the titanium band that it is difficult to disprove the possibility that it might be present to a small extent in the emission of materials containing no manganese (curve 1, Fig. 6); against this possibility are (*a*) the almost complete symmetry of the band in the absence of manganese, and (*b*) the acceptability of the sensitization theory to explain the general behavior of the materials. In other words, the small double peak seen when manganese is absent is not evidence of the presence of the "manganese" band, but it does suggest some kind of fine structure or double band in the titanium emission; compare the halophosphates, where the antimony band is double (6).

It should be noted that all the peaks mentioned are derived from curves of relative energy per unit frequency interval plotted against frequency. If the more usual curves of relative energy per unit wavelength interval against wave length are examined, the maxima are in somewhat different positions and the double peak becomes less evident (see Fig. 1). The original titanium band then has a peak at 5400 Å and the prominent manganese band moves from 5920 Å to 5990 Å. These values apply to both phosphors and lamps. The high red emission in the fluorosilicates is evidently due in large measure to the presence of emission bands of still longer wave length than the main one (see Fig. 7).

MECHANISM OF LUMINESCENCE

It is unusual to find that manganese can be incorporated in a titanium-activated phosphor (excited by ultraviolet); in most phosphors activated by titanium, manganese functions as an impurity quencher. For example, 0.1% by weight of manganese as manganese phosphate incorporated in barium titanium phosphate reduces the intensity of the fluorescence by about 50% without affecting the color of the emission (8). A similar effect is found with magnesium titanium borate (9). However, in former titanium-activated phosphors excited by ultraviolet radiation, the proportion of titanium is high, whereas in the present magnesium fluorosilicates the optimum proportion is about 0.015 at.%, and this difference may have a bearing on the difference in the function of manganese.

The known cases of sensitization in inorganic phosphors excited by ultraviolet radiation show a variable gap between the peak positions of the sensitizer and of the secondary activator. This difference is 13700 cm^{-1} for $CaSiO_3$·Pb, Mn; 13400 cm^{-1} for $Ca_3(PO_4)_2$·Ce, Mn; 8750 cm^{-1} for Ca halophosphate, Ag, Mn (10); about 7000 cm^{-1} for CaF_2·Ce, Mn (11); about 6000 cm^{-1} for $CaSrP_2O_7$·Sn, Mn (7); about 3700 cm^{-1} and 3000 cm^{-1} for chloro- and fluorophosphates, Sb, Mn, respectively (6). In the present phosphors the difference appears to be no more than 1300 cm^{-1}; in fact the two bands largely overlap, and this tends to obscure the nature of the mechanism. For efficient energy conversion between sensitizer and activator there is an advantage in proximity of the bands; thus, calcium silicates are not very efficient phosphors, while halophosphates are much more efficient. In the latter case, the bands of Sb and Mn overlap to a small extent, and it is suggested that still greater overlap in the fluorosilicates fails to yield the energy conversion advantage to the full because some of the quanta available from the sensitizer centers, if they correspond to the wide range of quanta which would otherwise be emitted as light in the 17700 cm^{-1} band, are too small to excite some of the emitting states in the manganese ions. That is, if anti-Stokes emission does not occur, there will be a loss of efficiency in the sensitization process. There is likely to be an optimum spacing of the two bands in terms of energy output, and this may possibly have been reached in the halophosphates, where the positioning of the bands in the spectrum is also favorable in relation to the spectral sensitivity of the eye.

Computations have been made to estimate the efficiency of energy conversion from the titanium band to the manganese bands. Measured efficiencies and spectral distributions of lamps were used, together with the standard colorimetric data; no account was taken of the possible nonavailability of some "Ti quanta" due to band overlap, but allowance was made for the unconverted proportion of the titanium band. For the phosphor of Fig. 7, the energy conversion is found to be about 65%, or a quantum conversion of 71%. If this last figure had been 100%, that is, if all the "Ti quanta" which had disappeared had reappeared as "Mn quanta," the lamp would have had an efficiency of 48 lpw instead of 39 lpw. A similar computation for experimental halophosphates containing fluorine but no chlorine, and alternatively antimony or antimony with manganese, gave higher values. The energy conversion appears to be about 100%, and the quantum conversion 110%. The latter cannot exceed 100%, and the figures therefore emphasize the approximate nature of the determination; but they also confirm that the halophosphate is, comparatively, a very efficient phosphor, in agreement with the suggestion made in connection with band positions.

Conclusion

In the past, titanium and manganese have appeared incompatible as activators (as distinct from titanium forming a component of the matrix) in phosphors excited by ultraviolet radiation to the order of efficiency required in fluorescent lamps. The magnesium fluorosilicate phosphors show that this is not always the case and seem to be the first example of joint activation by titanium and manganese.

Acknowledgments

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1956 Journal.

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Investigations of Surface Recombination Velocities on Germanium by the Photoelectromagnetic Method[1]

T. M. Buck and W. H. Brattain

Bell Telephone Laboratories, Inc., Murray Hill, New Jersey

ABSTRACT

The Photoelectromagnetic, or "Deathnium Meter," method has been used to detect changes in surface recombination velocity on germanium produced by various chemical surface treatments and by heating to temperatures of 65°–100°C. The method consists of measuring the open circuit voltage due to the P.E.M. effect. Measurements may be made rapidly; small changes in specimen thickness caused by a surface treatment may be ignored; the method can be used to investigate surfaces covered by opaque protective coatings. While it was found that the open circuit voltage depended on surface recombination in a manner which agreed qualitatively with theory, the agreement was not good enough to permit calculation of quantitative values of recombination velocity.

Introduction

It is widely recognized that surface properties of semiconductor materials have a very important influence on the behavior of semiconductor devices, and the surface recombination velocity is one of these important surface properties. Surface recombination and volume recombination control the lifetime of minority carriers in germanium (1); high recombination rates cause short lifetimes. A long lifetime is usually desired since, for example, this favors low reverse saturation currents in p-n diodes and high alphas in transistors. Therefore, a low and constant surface recombination velocity is ordinarily preferred.

The concept of surface recombination velocity arises from the fact that, for small concentrations of excess minority carriers, the rate at which these excess carriers recombine per unit area of surface is proportional to their concentration just below the surface. The constant of proportionality has the dimensions of a velocity and is called the surface recombination velocity, S (cm/sec).

The photoelectromagnetic method of measuring S used in the present work was proposed by workers at the Telecommunications Research Establishment. They had observed the photoelectromagnetic effect in germanium and then developed a theory which predicted that the effect could be applied to this measurement. The theory, together with experimental results for two types of germanium surfaces, chemically polished and lapped, has been reported on by Moss, Pincherle, and Woodward (2).

Kikoin and Noskov (3) observed the effect in cuprous oxide in 1934, while Aigrain (4, 5) and Bulliard (4, 6) have recently investigated the effect in germanium. These workers, however, did not apply it specifically to the measurement of surface recombination velocities in the manner of Moss, Pincherle, and Woodward.

The present work is concerned with the use of the method to detect changes in recombination velocity on germanium produced by various chemical surface treatments and by heating to temperatures of 65°–100°C. It is found that measurements may be made rapidly; small changes in specimen thickness caused by a surface treatment may be ignored; the method can be used to investigate surfaces covered by opaque protective coatings. It is felt that the method is quite useful for qualitative comparisons of surface treatments, as regards surface recombination. It should be emphasized, however, that the method is a qualitative rather than a quantitative measure of surface recombination velocity. This point is discussed later.

Experimental Method

The principle of the method is pictured in simplified form in Fig. 1 which represents a side view of a thin slab of germanium. The intense light shining on the front surface creates a high concentration of both holes and electrons at that surface; if S at this surface is not too large, most of them diffuse toward the dark side where they recombine at a rate determined by the recombination velocity there. Recombination in the interior is neglected since material of high body lifetime may be used and the thickness of the specimen kept less than a diffusion length. In the magnetic field the holes and electrons in the diffusion current tend to be deflected in opposite directions and this sets up a difference of potential, similar to a Hall voltage, which is the quantity measured.

This voltage, V_z, evidently depends on magnetic field strength and on diffusion current. Diffusion

[1] Manuscript received January 28, 1955. This paper was prepared for delivery before the Chicago Meeting, May 2 to 6, 1954.

current depends on the concentration gradient which, in turn, depends on the intensity of the light and on the recombination rates at the two surfaces. The Moss, Pincherle, Woodward theory predicts that, when recombination at the front surface is small, V_x should reach a saturation value at high light intensity and that under these conditions the equation

$$\frac{V_x}{l} = E_x = -\left(\frac{H}{C}\right) S$$

relates the voltage to the recombination velocity S at the back surface. H is the magnetic field strength (6400 gausses, in the present work); C is the velocity light; and l is the spacing between contacts.

In practice it is found that V_x does saturate at intensities approaching 10^{18} quanta/cm² sec. However, it now appears that the saturation effect may be due to heating of the specimen under the intense illumination. If readings are taken quickly enough so that no appreciable heating occurs, V_x continues to increase with intensity somewhat beyond 10^{18} quanta/cm² sec which is as high as the intensity dependence has been followed. Furthermore, as is seen later, the value of S for sand-blasted surfaces is not as high as previous estimates by other methods.

The determination of actual values of surface recombination velocity by this method must depend on a knowledge of the surface recombination mechanism. If one assumes that the process is governed by the mass action law, one would have

Net rate of recombination $= C\,(np - n_0p_0)$

where C is a constant determined by surface treatment, n and p are electron and hole concentrations, and the subscript zero denotes equilibrium values. The M.P.W. theory used the small signal approximation of this law, i.e., $np - n_0p_0 = (n_0 + p_0)\delta p$ for a situation where because of light intensity such an approximation does not hold. Unfortunately, if one assumes the mass action law without approximations, the theory becomes much more complicated and difficult to test experimentally.[2] In addition, the question of whether this law is the correct one arises. Furthermore, it should be pointed out that, if this law is correct, one would expect S for a given surface treatment to vary with hole and electron concentration (7), other things being constant. Thus, the values of S quoted in this paper apply only to material of the specified resistivity.

Nevertheless, while the absolute values of S are in some doubt, experiments show that V_x values do vary in the proper direction with recombination velocity, and that the method is useful for comparing surface treatments. For example, in Fig. 2 V_x is plotted against etching time. The downward curve

[2] The authors are indebted to W. van Roosbroeck, of this laboratory, for having investigated this.

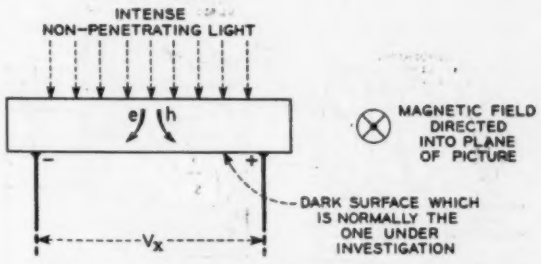

FIG. 1. Photoelectromagnetic method of measuring surface recombination velocity. Schematic diagram of principle of operation.

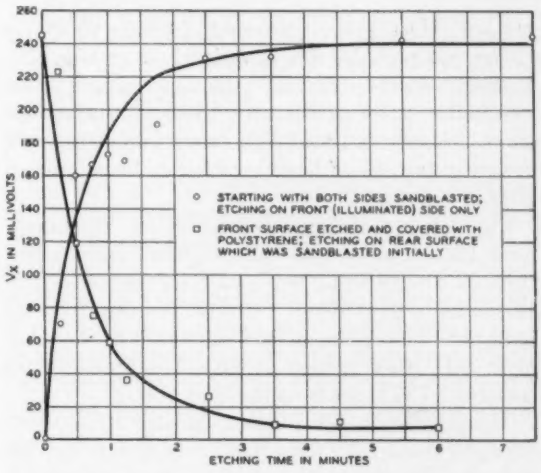
Vx IN MILLIVOLTS
ETCHING TIME IN MINUTES
STARTING WITH BOTH SIDES SANDBLASTED; ETCHING ON FRONT (ILLUMINATED) SIDE ONLY
FRONT SURFACE ETCHED AND COVERED WITH POLYSTYRENE; ETCHING ON REAR SURFACE WHICH WAS SANDBLASTED INITIALLY

FIG. 2. Change of V_x as a function of etching time on a sandblasted surface. CP-4 etchant. Measurements in dry nitrogen atmosphere; p-type germanium specimen; 13 ohm-cm, 2000–3000 μsec body lifetime.

shows the case where initially the illuminated surface was chemically etched and the dark side sand blasted, giving a value of 240 mv corresponding to about 2000 cm/sec by the M.P.W. theory. (Estimates of at least 10^4 cm/sec are usually made for such a surface.) A series of short chemical etching treatments on the back surface (10–15 sec each) brought V_x down progressively until it became substantially constant at about 15 mv, or 135 cm/sec.

In the upward curve of Fig. 2 both the front and back surfaces were sand blasted initially, leading to a V_x value of only a fraction of a millivolt since most of the carriers created by the light recombined at the front surface and there was little or no concentration gradient or diffusion current. The front surface, only, was then given several brief (10–15 sec) chemical etches; V_x increased with each treatment until a value of about 240 mv was reached, i.e., with each etching treatment recombination at the illuminated surface decreased and the diffusion current to the high recombination sink at the back surface in-

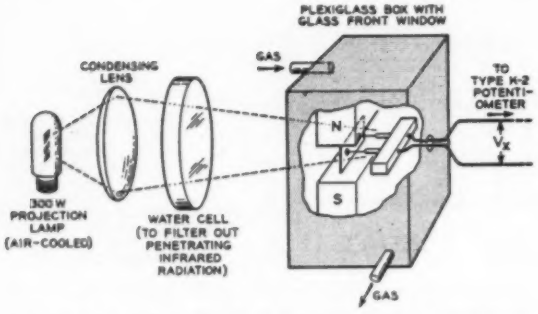

FIG. 3. Schematic diagram of apparatus for photoelectromagnetic measurement of surface recombination velocity.

creased. Most of the scattering of points about the curves was probably due to variation in etching rate. Hereafter in the discussion the dark surface is the one under investigation with the front surface assumed to stay constant at a fairly low value of S, except in the case of heating effects to be mentioned later.

Fig. 3 is a schematic diagram of the equipment used. Light from the 300-watt projection lamp passed through a condensing lens and then through a 1.5-cm water cell to remove the penetrating infrared radiation. The specimen was supported in the magnetic field (6400 gauss) by phosphor bronze wires soldered 1.75 cm apart on the back surface.

The germanium specimens used were 10–15 ohm-cm slabs about 2.5 x 0.8 x 0.05 cm in dimension, the thickness being considerably less than a diffusion length since body lifetime was 2000–3000 μsec.

RESULTS

Chemical treatments.—Table I shows results of comparisons among a few surface treatments which have been used by various workers at this laboratory. In some cases both surfaces received the treatment, while in others the chemically etched front surface was covered by a thin coat of polystyrene to protect it from the treatments. According to the M.P.W. theory, small changes at low values of S on the front surface should have a negligible effect on V_x; rather V_x should be determined by the recombination velocity at the back surface which is under investigation. This seemed to be borne out in the experiments. However, it is preferable, if possible, to operate with the front surface sealed off by a transparent plastic coating. This is especially important when a surface treatment may be a very bad one because, as shown in Fig. 2, a very high recombination velocity on the front surface can cause a low response. That is, when both surfaces are exposed to an unknown treatment, a low reading may mean a good back surface or a very poor front surface.

The specimens were re-etched in CP-4 and washed in distilled water to present a fresh surface for each new treatment. All of the treatments were followed by a distilled water rinse.

The HF dip produced, temporarily, a reading as high as for sand blasting, in accordance with the findings of Keyes and Maple (8). Values for the last three treatments in the table fell in the same order for all four specimens. Thus the method seemed capable of detecting small but reproducible differences among the treatments. Values for CP-4 seemed less stable and reproducible than those for the other treatments; the KOH electrolytic etch seemed especially good in this respect.

Fig. 4 shows how V_x changed as the two p-type specimens received the series of treatments.

Heat effect.—It has been mentioned that the method employs nonpenetrating light of high intensity. Heating of the specimen by the light causes some trouble in the measurements. V_x readings were taken on the type K-2 potentiometer a few minutes after illumination to allow the specimen to reach thermal equilibrium at about 35°C. During this waiting period V_x settled down to a fairly constant value several millivolts lower than would be obtained immediately after illumination. (Recently it has been found more satisfactory to take readings quickly enough, by trial and error, so that no appreciable heating occurs.)

Aside from this transient effect, heating to temperatures much higher than 35°C should be avoided. For example, if the water filter is removed the sample then heats to about 65°C and if the light is left on for a few minutes a rather large increase in V_x occurs,

TABLE I. *Photoelectromagnetic measurements for various surface treatments on germanium*

Treatment*	V_x (mv)	S (Recombination velocity at dark surface, cm/sec) calculated from M.P.W. theory	
Sand-blasted (back surface, 180 mesh silicon carbide)	240	2160	
5 min HF dip after (8) thorough etching in CP-4	240	2160	
KOH electrolytic etch	17.8	160	averages of eight treatments on four specimens, two n-type and two p-type.
Antimony oxychloride —"Long Life" treatment	23.4	210	
Nitric acid soak	26.7	240	

* CP-4 is a mixture of 15 ml glacial acetic acid, 15 ml HF, 25 ml conc. HNO_3, and a few drops of bromine. A 0.1% solution of potassium hydroxide in distilled water was used in the electrolytic etching; the current density was about 50 ma/cm^2 and the electrolysis was continued for 2 min. The antimony oxychloride "long life" treatment consisted essentially of making the specimen anodic in a suspension of hydrolyzed Sb Cl_3 for 8 min, at 1½ v.

as measured with the filter in place again. This increase persists after the filter is replaced but V_x decreases toward the original value over a period of hours or days. Fig. 5 shows how a specimen behaved over a period of several days. Each time the specimen was exposed to unfiltered light (as indicated by the arrows) V_x increased, as measured with the filter in place again, and then slowly decreased with time although it usually did not return completely in the waiting period. This effect was also produced by heating in an oven at 70°–100°C. The same type of behavior was observed with a p-type specimen. Haynes and Hornbeck (9) had observed that recombination velocity was increased by heating to temperatures of less than 100°C in other lifetime measurements on germanium; it was therefore thought that the increase in V_x in the P.E.M. measurements was due to an increase in S.

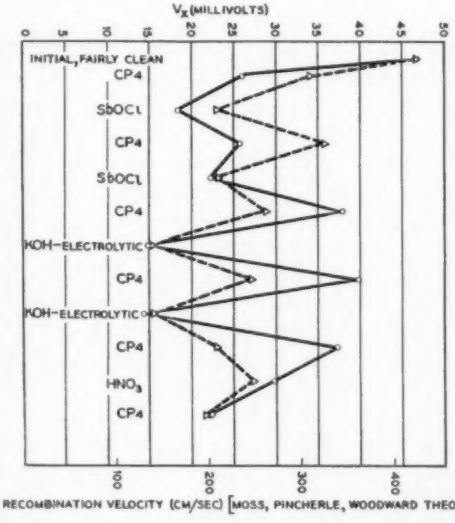

FIG. 4. Change of V_x as two p-type germanium specimens received a series of surface treatments. △ Specimen A, p-type 13 ohm-cm; ° Specimen B, (p-type) 13 ohm-cm.

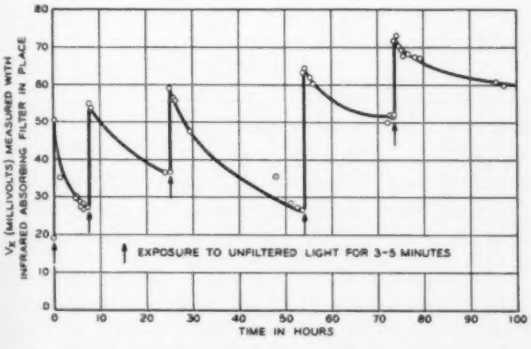
V_x (MILLIVOLTS) MEASURED WITH INFRARED ABSORBING FILTER IN PLACE
EXPOSURE TO UNFILTERED LIGHT FOR 3–5 MINUTES
TIME IN HOURS

FIG. 5. Effect of heating by exposure to intense unfiltered light. n-Type germanium, 11 ohm-cm. Measurements by photoelectromagnetic method in room air at ∽ 45% R.H.

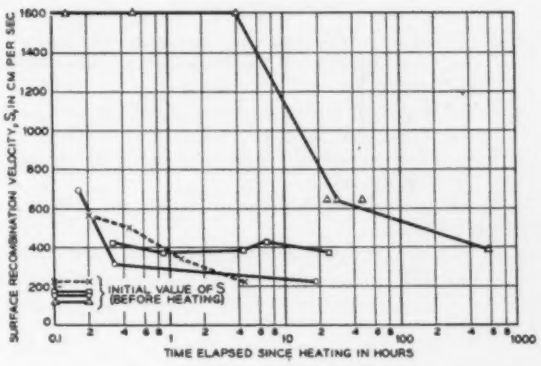

FIG. 6. Effect of heating on recombination velocity of germanium. Recombination velocity calculated from diffusion length measurement of filament lifetime. ° Specimen A (n-type) exposed to intense light for 5 min (as in photoelectromagnetic experiments). x, Specimen A illuminated again. △, Specimen A heated in oven at 100°C for 15 min. □, Specimen B (n-type) heated in oven at 100°C for 15 min.

To check this, the effect of heating was followed by diffusion length measurements of lifetime on thin rods of n-type germanium. This method has been described by Goucher (10). The results are shown in Fig. 6 in which S, computed from diffusion length, is plotted against time elapsed since heating. It is seen that the recombination velocity increased each time a specimen was heated, either by exposure to the unfiltered light used in the photoelectromagnetic experiments or by heating in an oven. There was considerable variation in the magnitude of the effect, possibly because of differences in atmospheric contamination during heating.

Parallel effects were also observed in few unprotected diodes and in an n-p-n grown junction transistor. In the diodes heating to 100°C for a total of 30 min caused an increase at room temperature of 30–50% in the reverse saturation current while the transistor exhibited an increase in $1-\alpha$ of over 60%.

In all cases the effect seemed to be temporary, disappearing gradually on standing in air. The heat effect experiments described were all carried out in room air usually controlled at 50% relative humidity or less. As yet the authors have no definite explanation for this behavior, although differences due to changing the ambient atmosphere have been noticed.

ACKNOWLEDGMENT

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1956 JOURNAL.

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Electrodeposition of Titanium on Base Metals[1]

M. E. Sibert and M. A. Steinberg

Horizons Incorporated, Cleveland, Ohio

ABSTRACT

A method for electrodeposition of protective titanium coatings on steel and other base metals is described. The procedure involves electrolysis of potassium titanium fluoride dissolved in alkali or alkaline earth halides under an inert atmosphere. Graphite or titanium metal anodes are employed.

Adherent titanium coatings up to 0.005 in. (0.127 mm) thick are produced. Coatings are essentially pure titanium. Underlying the coating is a base metal-titanium alloy layer producing a firm metal-metal bond. Coatings so prepared possess the corrosion resistance of titanium metal. Layers heavier than 0.005 in. (0.127 mm) may be prepared by repeating the process.

Equipment and materials used, conditions of operation, and properties of the electrodeposited titanium are described completely.

Introduction

Titanium is a useful corrosion resistant material under many conditions. However, its use is limited because of its relatively high cost. In many cases, a thin protective layer of titanium over a base metal would be adequate. At present, there are no methods available for application of such coatings other than pressure-roll-diffusion cladding which also suffers from a relatively high cost disadvantage.

A research program was initiated with the goal of developing methods for electrodeposition of titanium on steel and other base metals. The work was confined to fused salt electrolysis since it is doubtful that titanium can be isolated in aqueous or other oxygen containing media. Previous work has characterized titanium as a highly oxyphillic element. For this reason, all work was carried out under an inert atmosphere.

There are few recorded attempts to deposit titanium electrolytically on base metals. Most electrodeposition work has been done in aqueous media, and as such is open to question. Attempts have been made to duplicate some of this experimental work, but these efforts have been unsuccessful in terms of reported results.

Gratsianskii and Vovkogon (3) reported deposition of titanium films 1μ thick on copper from solutions of sulfanilic acid and titanium hydroxide. Platinum and zinc-titanium anodes were used. Cathode current densities of 0.1 amp/dm^2 at 20°C were recommended.

Haissinsky and Emmanuel-Zavissiano (4) claimed deposition of thin black titanium films from titanium dioxide in sulfuric acid and $Na_2SO_4 \cdot 10H_2O$ at a *p*H of 1.2–1.6. Such coatings contained 0.1–0.2 mg Ti/cm^2. They were produced using a lead cathode and platinum anode with a cathode current density of 1.5–2.0 amp/dm^2. Higher currents were said to precipitate titanium(IV) hydroxide. Similar plates were obtained on zinc and antimony, but results were negative with nickel and platinum. They also reported a plating method using titanium(III) sulfate solutions (5).

Pokorny and Schneider (7) obtained a patent on electroplating of titanium from a strongly alkaline solution of titanium dioxide or titanium(IV) hydroxide on iron or copper cathodes.

Leutz (6) obtained a patent on a process for electrolytically forming protective layers on base metals by anodic treatment in a bath containing a colloidal suspension of silicon, zinc, titanium, aluminum, or rare earth oxide and acid. An anion capable of forming an insoluble salt with the metal to be treated must be present.

Russell (8) reported a method of depositing titanium on noble metals by battery action which he also claimed to be valid for uranium, tungsten, and molybdenum. Acidified solutions of a salt of the metal to be plated are shaken with the noble metal. Mercury is specifically mentioned as a noble metal.

Gratsianskii and Vovkogon (3) also reported electrodeposition of titanium as a zinc alloy from a bath of aluminum chloride-sodium chloride-sodium fluoride. A 60-40 zinc-titanium alloy surface on iron or copper was produced at 300°C under 0.5 amp/dm^2 current density using a zinc-titanium anode.

Fischer and Dorsch were granted a patent on a fused salt titanium electroplating process (2). Again, alloys were produced by electrolysis of fused mix-

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tures of alkali or alkaline earth halides and titanium halides. Such baths were operated above the melting point of the alloy to be formed and below the melting point of the alloying cathode metal.

Recently, Brenner and Senderoff (1) reported formation of 0.5 mil adherent layers of titanium on tungsten by electrolysis of titanium(III) chloride in a mixture of sodium chloride and potassium chloride. Such layers were formed at 900°C and at 30 amp/dm².

Schlechten, Straumanis, and Gill (9) have described the deposition of titanium coatings from pyrosols of titanium. The pyrosols were formed from titanium metal and fused alkali or alkaline earth chlorides. Coatings up to 7 mils were obtained on copper and iron, but these were essentially alloys.

There are several choices of procedure: a titanium bearing material may be electrolytically decomposed; a soluble metal anode might be used with a carrier salt; or a pyrosol might be used. The first approach was used in this investigation.

The choice of a source electrolyte was reasonably limited due to the assumed requirement for a stable anhydrous, oxygen and nitrogen free salt. It must also be a good electrical conductor, thus ionic in nature. A common source material meeting these requirements is potassium titanium fluoride. It is readily prepared by standard chemical techniques and may be handled in air, although it is readily oxidized at elevated temperatures.

In order to obtain a melt at reasonable temperature, the source electrolyte is diluted, preferably with another halide. Furthermore, the double fluoride is not readily reduced as a pure melt.

In this process, a suitable melt of K_2TiF_6 dissolved in a second halide is electrolyzed to reduce the K_2TiF_6 and cathodically deposit thin layers of titanium on steel parts. The process is a rapid, high current procedure resulting in an adherent diffusion bonded titanium layer. Details of the procedure are given below.

Experimental

The Electrolytic Cell

Titanium was electrodeposited in a cell specifically constructed for high temperature inert atmosphere electrolysis. The cell takes a salt charge of 5 lb in a crucible 4 in. (10.2 cm) in diameter x 8 in. (20.3 cm) deep. Equipment of similar design has been previously described in detail (10).

Electrolytic Procedure

The process was essentially an electrolysis of a K_2TiF_6-NaCl melt with the material to be plated used as a cathode. The salt bath was chosen on the basis of favorable operating characteristics. Pure K_2TiF_6 was not readily electrolytically reduced to metal because of the high titanium ion concentration and consequent ease of reoxidation. However, when the salt was dissolved in melts of alkali or alkaline earth fluorides and chlorides, the reduction proceeded with varying degrees of success. Fluorides were not generally suitable because of their insolubility. Some of the salt bath adhered to the cathode and was best removed by aqueous washing. Alkaline earth chlorides were undesirable because of their hygroscopic nature and the difficulty in drying them. Considering both chemical and economic aspects, lithium chloride, sodium chloride, and potassium chloride were the most useful bath materials. Since sodium chloride was readily available in pure anhydrous form and also behaved well electrolytically, it was employed for most of the work.

All salts were of AR grade or equivalent. The K_2TiF_6 was twice recrystallized and usually vacuum dried to remove residual moisture.

Cathodes to be plated were, for the most part, machined from ingot iron. In some cases cold rolled steel was used. Cathodes were in the form of bars, cylinders, or truncated cones. To further insure a clean surface, the cathodes were washed in carbon tetrachloride, then pickled in 20% hydrochloric acid -10% nitric acid for 20 min, followed by rinsing and drying.

The cell, in clean condition, was first heated to 850°–950°C with a thorough argon flushing. The salts were then charged and melted over a period of 30–45 min.

After the temperature had been adjusted, any additional desired bath purification was carried out. A low voltage pre-electrolysis may be used to remove residual moisture and/or other impurities. Graphite or steel cathodes may be used; any deposit is discarded.

The cathode assembly was then lowered into the melt. Cathodes were generally attached to nickel rods by means of welding or clamping. The rod, in turn, was protected with a graphite sleeve. The current was then applied, voltage adjusted, and electrolysis carried out for the desired number of ampere hours, during which time some chlorine was evolved anodically.

For most of the work a 15–17% K_2TiF_6 concentration in sodium chloride was employed as the melt. This gave a mixture melting at about 720°C and having a convenient fluidity at the usual electrolysis temperature range of 850°–950°C. Such a bath provided available titanium (approximately 68 g) for a large number of cathodes. It was possible, however, to operate successfully a bath containing between 5–25% K_2TiF_6.

TABLE I. *Operating conditions for titanium electroplating of steel*

Run	Type K_2TiF_6	Other agents	Temp, °C	Current density amp/dm²	Volts	Amp hr	Time min	Cathode	Results	Remarks
								in. ingot iron		*Run on bath*
1–4	Recryst. (wet)	H_2O	905	86	6.1	67	80	¼ × 1 × 3½	Good clad 0.002 in. (0.051 mm)	Fourth
2–6	Recryst.	—	910	81	5.7	67	80	¼ × 1 × 3¾	Excellent 0.003 in. (0.076 mm)	Sixth
3–2	Recryst. vac. dried	1% TiO_2	810	475	—	67	20	¼ × 1 × 2½	Very good 0.004 in. (0.102 mm)	Second
4–1	Recryst. vac. dried	1% TiO_2	810	345	13.5	67	20	¼ × 1 × 3½	Very thin	First
5–1	Recryst.	H_2O	770	345	14	67	20	¼ × 1 × 3½	Spotty	First
6–3	Recryst. vac. dried	—	885	480	8.3	93	20	¼ × 1 × 3½	None	Third

After electrolysis, the cathode was withdrawn from the melt with voltage on it to prevent solution of the titanium electroplate. It was then allowed to cool in the argon atmosphere above the bath or in a cooling chamber (argon filled) which may be used as a cell accessory. The cathode was washed in water to remove the salt coating and some crystalline metal. A typical washed plated specimen has a bright finish and resembles common electroplated materials.

Electrolysis Experimentation

A variety of conditions have been imposed on the basic process in order to elucidate the optimum conditions of operation. Almost from the first run, evidences of cladding were detected, but results were sporadic and nonuniform. Temperature, voltage, current, and type of titanium source electrolyte were varied and studied.

In this process, voltage, type of cell feed, and temperature were the principal contributing factors. Data for typical runs illustrating operating conditions are given in Table I. The first three runs illustrate satisfactory deposition conditions. The fourth run was unsatisfactory due to excessive voltage and consequent codeposition of sodium. The fifth run was poor from this same standpoint and also was operated at too low a temperature. In the last run, the cathode was not properly cleaned, and the voltage was somewhat high.

In each electrolytic run, plating took place early in the run and the process terminated. Continued electrolysis produced a porous crystalline deposit around the cathode, but no further electroplating. However, if the cathode was cleaned and the process repeated, the thickness of the coating was increased.

In a typical multiple electrolysis, a bar 0.246 in. (6.24 mm) thick was plated at 5.7 v and 95 amp/dm² at 910°C using a 16% K_2TiF_6-NaCl melt. After one run the thickness was 0.252 in. (6.35 mm). The bar was withdrawn, washed, and replated four times until the thickness was 0.262 in. (6.65 mm). This yielded a total plate 0.008 in. (0.20 mm) thick or an average of 0.0016 in.(0.04 mm)/pass.

The presence of impurities in the melt was a factor of some significance. It was indicated initially that small additions of titanium dioxide or the use of incompletely dried K_2TiF_6 (which would yield oxides on melting) improved the characteristics of the titanium electrodeposition process.

A small amount of titanium oxide, either titanium dioxide or Ti_2O_3, was helpful and possibly necessary to obtain successful electrocladding. It was known that all melts contained some moisture initially as contributed both by the K_2TiF_6 and sodium chloride. This averaged about 0.01–0.02% by weight. Thus, some oxide was undoubtedly present in all such runs and as such was a contributing factor. It was also demonstrated that such oxides are not reduced to metal or to titanium monoxide in a melt of sodium chloride and K_2TiF_6. It is probable, therefore, that Ti_2O_3 or titanium dioxide present initially remained in the melt over a substantial period of time through a cycling redox process, even when low voltage purification electrolyses were carried out. Therefore, it was quite possible for oxides, either initially in the melt or deliberately added, to play a part in the electrocladding process.

It was possible that oxygen here played somewhat

TABLE II. *Effect of cell feed on titanium electrodeposition*

Run No.	Treatment K_2TiF_6	Bath Additives	Thickness of Ti Coating	Remarks
1	Recryst. no drying	—	0.003 in. (0.076 mm)	H_2O—0.1% in melt after run
2	Commercial vac. dried	—	0.003 in. (0.076 mm)	245 Amp-hr run
3	Bath from 6 (see below)	—	0.0025 in. (0.064 mm)	0.13% H_2O at start electrolysis
4	Recryst. air dried	1% TiO_2	0.002 in. (0.051 mm)	150 Amp-hr low voltage electrolysis
5	Recryst. vac. dried	—	0.001 in. (0.025 mm)	
6	Recryst. (wet—from filter)	20% H_2O start	Spotty	
7	Commercial vac. dried	—	None	

TABLE III. *Effect of bath temperature on electrodeposition of titanium*

Run	Temp °C	Volts	Current density amp/dm²	Total amp-hr/dm²	Cathode type	Cladding results	Remarks
1	765	3.0	120	40	Mild steel truncated cone	None	Bath pre-electrolyzed
2	755	6.6	485–240	640	Mild steel truncated cone	None	
3	770	14	345	115	Ingot iron bar	Spotty	Wet K_2TiF_6—1st run
4	875	3.0	120	29	Truncated cone	Thin	
5	885	6.3	485	198	Truncated cone	Good	TiO_2 in bath
6	900	—	345	345	Ingot iron bar	Heavy	Wet K_2TiF_6—3rd run
7	905	5.9	86	115	Ingot iron bar	Excellent	Wet K_2TiF_6

the same role as sulfur in electroplating processes. Additives in the form of sulfonates are frequently made to plating baths to produce fine grained smooth deposits. Indications are that deposits produced in such a manner contain appreciable sulfur; maximum sulfur concentrations are noted at the points of high current density, indicating that the additive may deposit at such points and divert the current to other areas, thus producing a uniform smooth deposit. Since oxygen has a similar electronic configuration to that of sulfur, it may be that a comparable action took place in titanium electrodeposition.

The data in Table II illustrate the effects of adding titanium dioxide and moisture to the salt melts. Runs are arranged in approximate decreasing order of effectiveness of the cell feed. The use of commercial or recrystallized K_2TiF_6 in a freshly dried state (runs 5 and 7) produced poor deposition or none at all; however, after one run on a bath and its subsequent standing overnight, which exposed it to some back diffusion of air and normal cell leakage, the second run (run 2) produced good results. Runs 1 and 4 are illustrative of results obtained by adding nominal amounts of moisture and titanium dioxide to the melt.

Temperature had a definite effect upon the process. The fluotitanate was reduced to metal over a considerable temperature range, but poor plating was obtained below 800°C. Coatings were not continuous and were subject to peeling. Plates obtained at 800°–900°C had a diffusion bond of titanium and base metal between the base metal and titanium layers. This bonding area was high in base metal content, and, in the case of iron, gave a typical stabilization of the β titanium phase in this area. The layer over this bonding area was normal α titanium. Such a bond is highly desirable from an adherence standpoint, and it is apparent that temperatures of the order of 800°C are required to produce this type of bonding. Evidence indicates that plating took place at lower temperatures, but that the diffusion rate of iron into titanium was not sufficiently rapid to effect a good bond, so the plates tended to flake off in the relatively corrosive atmosphere of the K_2TiF_6-NaCl melt.

Voltage was important in its relation to the decomposition voltages of the bath constituents. No titanium was produced at less than 1.8 v in this cell. The decomposition voltage of sodium chloride is about 3.1 v at 850°C, but as long as an appreciable titanium concentration (0.5% or more) existed in the bath, no sodium was produced up to 5.5–6.0 v. Thus, the bath was operated at about 3–6 v. Current density did not seem to be an important variable between the limits of 50–500 amp/dm².

Table III gives a tabulation of typical runs showing effects of temperature. It is noted from these runs that no particular effects are evident from voltage and current variation, cathode geometry, and time within the stated limits.

It is evident from the data in Table III that the higher temperatures were requisite for successful operation of the process. At temperatures under 800°C, variations in voltage, current, and type of cathode produced either poorly coated specimens or no coating. On the other hand, well clad specimens resulted at the higher temperatures regardless of current, voltage, and type of cathode.

As a final check on the process, electrodeposition of titanium on standard nuts and bolts was attempted. These were welded or bolted to standard nickel cathode rods and the process carried out as for other cathodes. Some difficulty was experienced in

TABLE IV. *Electrocladding of commercial bolts*

Run	Cathode	Voltage	Current Amp	Temp °C	Ti coating	Remarks
1	Cold-rolled ½ in. bolt	3.0	50	955	Poor	Rusted in brine
2	Cold-rolled ½ in. bolt	5.6	200	977	Coated	Some alloying
3	Cold-rolled ½ in. bolt	5.5	200	855	Coated	
4	Cold-rolled ¼ in. bolt	2.6	20	845	None	
5	Cold-rolled ⅜ in. bolt	2.5	35	855	Good	No attack 20% HNO_3

getting good coatings inside the threads, presumably due to the differential in current density over the ridges. Coated specimens were obtained, but results were not entirely consistent. Typical runs are listed in Table IV.

Corrosion Testing of Cathodes

Most of the various coated specimens produced (rods, bars, cones, and bolts) have been corrosion tested by several methods: 20% and concentrated nitric acid, 20% and concentrated hydrochloric acid, concentrated sulfuric acid, and 20% sodium chloride solution.

In general, all cathodes which appeared evenly coated were comparable to titanium metal in their resistance to all acid and basic media for periods up to 3 months. In some instances, thin spots were revealed by the brine test, particularly in the case of threads on the bolts. Fully coated bolts, however, were obtained.

This is a case where a large adjustment in current density might have had some effect. The ridges of the threads were well covered, these being the points of maximum current density, but the troughs were coated only thinly or not at all.

One corrosion test which is representative of electrodeposited bar specimens involved soaking in a 20% nitric acid solution for 27 days (648 hr). A washed cathode specimen was selected measuring 0.751 in. (1.91 cm) wide x 0.268 in. (0.68 cm) thick. After 27 days, there was no detectable change in measurement of the sample.

Physical Examination

A large number of titanium coated specimens were examined metallographically. This conclusively established the nature of the process and the type of bonding obtained. It was a measure of the uniformity and thickness of the titanium coatings prepared.

Fig. 1 is illustrative of a typical electrodeposited titanium layer. A section of the cathode is shown under polarized light delineating the transition structures. From the surface are the α titanium area (where grains are evident), β titanium high in iron, a thin intermetallic area (probably TiFe), and a high iron alloy bond merging with the matrix.

Identification of these phases was confirmed by x-ray analysis. Fig. 2A is an x-ray reflection pattern from the surface of the specimen in Fig. 1 showing an α titanium structure. Fig. 2B is from a thin deposit and shows β titanium lines. The pattern in Fig. 2C contains both α and β titanium lines as shown by a coating of medium thickness. For comparison, the pattern of commercially pure titanium is shown as Fig. 2D.

The electrodeposits in Fig. 3–5 were all prepared

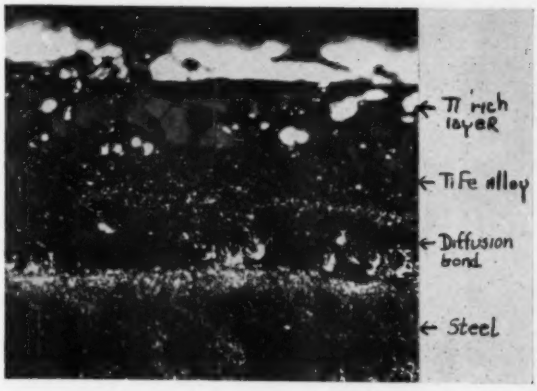

FIG. 1. Typical titanium electrodeposit on mild steel. (250× before reduction for publication)

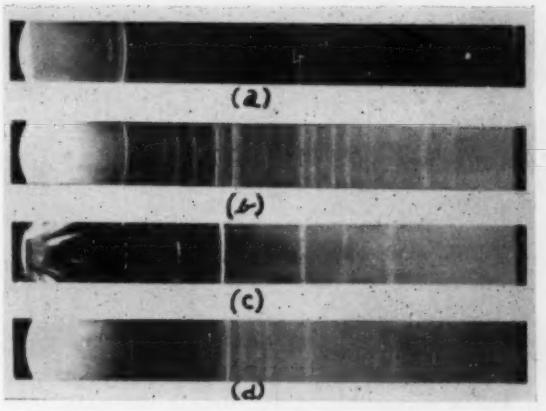

FIG. 2. X-ray patterns of electrodeposited titanium. (a) Surface of specimen in Fig. 2. (b) Thin coating showing β titanium lines. (c) Intermediate coating showing α and β lines. (d) Commercial titanium pattern.

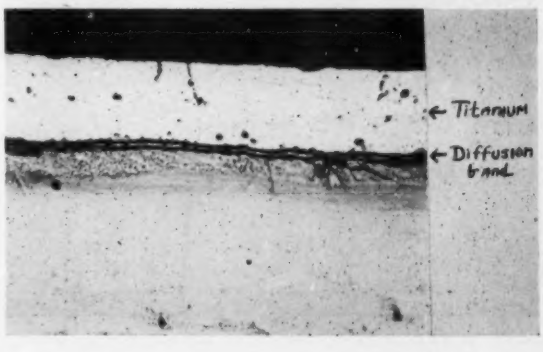

FIG. 3. Heavy coating on ingot iron bar. Etched in HF-HNO_3-glycerine. (500× before reduction for publication)

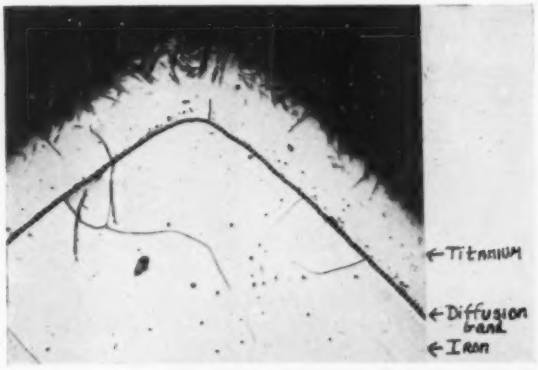

FIG. 4. Thin coating (<0.001 in.) on ingot iron bar; corner of sample; etched HF-HNO_3-glycerine. (250× before reduction for publication)

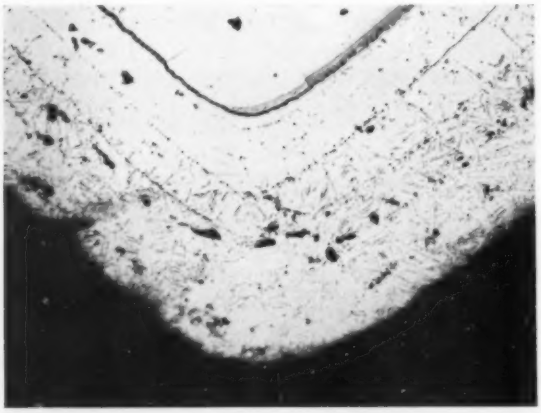

FIG. 5. Corner view of five titanium layers electrodeposited on ingot iron. (250× before reduction for publication)

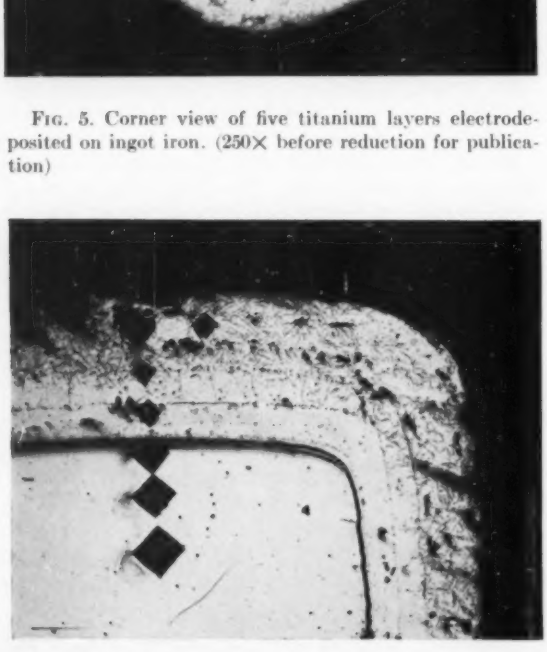

FIG. 6. Multiple layer specimen showing microhardness impressions. Etched in HF-HNO_3-glycerine. (250× before reduction for publication)

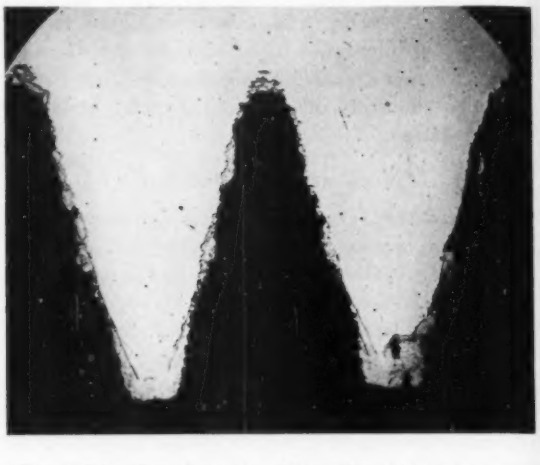

FIG. 7. Titanium electrodeposit on threaded bolt section

at 800°–950°C and show an iron-titanium interface stabilizing the β titanium phase. There is some variation in porosity in such a group of specimens, but the porosity is never continuous through the deposit to base metal. Fig. 3 and 4 illustrate the variation in thickness of deposit which may be obtained. Characteristics of the bond and surfaces are the same.

Fig. 4 and 5 illustrate the uniformity of deposits obtained at the corners of specimens.

Fig. 5 is of particular interest, illustrating five separate layers produced from five separate repetitive runs. The thickness of each individual layer is evident from the faint lines in the coating parallel to the surface. Fig. 6 is the same specimen showing microhardness impressions taken on various layers of the sample. A Vickers pyramid with a 25 g load was used for these measurements. From surface to the center, readings of 352, 383, and 340 VPN were obtained for the titanium and 167, 119, and 80 VPN for the iron.

In comparing Fig. 1 with Fig. 3, it is observed that a coating applied to mild steel has a thicker boundary phase than for ingot iron. This layer is thought to be a titanium carbide or perhaps an oxycarbide, since it is associated with decarburization of the base metal.

Fig. 7 is a longitudinal section of a threaded bolt electrodeposited witb titanium. The coating is less uniform than those obtained on bars or cylinders, but does provide corrosion protection to the threads.

DISCUSSION OF RESULTS

It was established that steel can be plated by electrolytic means, and consistently good results were obtained on simple surfaces. A fused bath of sodium chloride and K_2TiF_6 was satisfactory; lithium chloride or potassium chloride could be used

with equal success in place of sodium chloride. A protective atmosphere was a requirement as was an inert container for the melt.

A low voltage pre-electrolysis to remove impurities was of no special advantage to the process, i.e., it did not guarantee a successful run. Presumably, pre-electrolysis did assist in removal of excess moisture and other minor impurities which had decomposition voltages under that of K_2TiF_6. It is doubtful that such a procedure effectively removed titanium dioxide or Ti_2O_3 from a NaCl-K_2TiF_6 melt.

An increase in temperature up to 950°C benefited the electrodeposition action. Temperatures much greater than this caused incipient melting rather than a diffusion bonded electroplate. Voltage was not a critical factor and was varied between 3 and 6. Current density was even less significant, good runs resulting at 50–500 amp/dm^2.

Bath concentration was not extensively investigated, but it is known that the system NaCl-K_2TiF_6 is operable as an electrolyte in the range 5–25% K_2TiF_6. Sixteen per cent K_2TiF_6 produced a mixture of convenient melting range and provided a metal/bath weight ratio of 3/100, making any one bath suitable for treatment of a large total area of base metal surface.

The exact time required for deposition at a given current was not well established, but it is known to be relatively short. If a cathode was left in the bath for longer than 10–15 min at 80 amp/dm^2, a heavy build-up of crystalline titanium resulted. A 3¾ in. x 1 in. x ¼ in. (9.52 cm x 2.54 cm x 0.64 cm) steel bar was coated at 35 amp-hr in 10 min.

Heavier coatings were prepared by removing the cathode, cleaning it, and repeating the process. It was not shown why the plating process stopped after a relatively short time and was succeeded by crystalline deposition. However, the fact that the plating could be continued after cleaning was indicative that such behavior was associated with either the cathode surface or the area immediately adjacent to the cathode. A small volume of salt was removed with the cathode and discarded during the washing. This may have served to deplete the cathode area of a high concentration of depositing ions, enabling further plating rather than dendritic crystal growth. Similarly, such a cleaning procedure might remove codepositing impurities which could serve as nuclei for crystal growth on the cathode surface.

Hard, adherent, titanium coatings were produced by this method. There was no tendency toward peeling or exfoliation. The coatings were ductile enough to permit rolling or working of the original cathode.

Bend tests were conducted on coated samples having a 1 in. x ¼ in. (2.54 cm x 0.64 cm) cross section, and the titanium surface layer cracked after very slight plastic extensions of approximately 1%. However, it was noted in these tests that the adherence of titanium to the ingot iron base material was excellent. In free bend tests no peeling of the coating occurred after bending specimens flat upon themselves (bend radius of about ½ the thickness of the sample). These films were generally 0.001–0.003 in. (0.025–0.076 mm) thick, but could be increased by repeated electrolysis.

Summary

A process was developed whereby thin titanium layers were bonded to steel or other base metals by fused salt electrolysis involving the use of a fused NaCl-K_2TiF_6 mixture. It was a rapid, inexpensive process, since high currents and voltages were employed and only a small amount of titanium was involved. The electroplated layer completely protected the coated article with all the corrosion resistance properties of titanium itself. The titanium layer was firmly bonded to the base metal by an alloy interface.

Consistently good results were achieved using cathodes of simple geometry. Articles such as nuts and bolts were more difficult because of the areas of varying current density, but this can be overcome.

Acknowledgment

The authors are grateful to the Wright Air Development Center for support of this work and permission to publish the results.

The authors also acknowledge the work of the following in carrying out this research effort: G. J. Franke, R. H. Baskey, F. C. Wagner, and B. C. Raynes, all of Horizons Incorporated.

Any discussion of this paper will appear in a discussion section to be published in the June 1956 Journal.

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Liquidus Curves for Aluminum Cell Electrolyte

I. Cryolite-Alumina[1]

N.W.F. Phillips, R. H. Singleton,[2] and E. A. Hollingshead

Aluminium Laboratories Limited, Arvida, Quebec, Canada

ABSTRACT

Liquidus curves for the system cryolite-alumina up to 1050°C and 16% alumina were determined by means of cooling curves and visual examination of the cooling melt. The freezing point of pure cryolite was 1009° ± 1°C, and the cryolite-alumina eutectic point was at 962°C and 10% alumina (weight per cent). On the alumina side of the eutectic point, crystallization was sluggish, and there was no break in the cooling curve corresponding to the first appearance of crystals in the melt.

Introduction

Aluminum is produced commercially by the electrolysis of alumina dissolved in molten cryolite with minor additions of other salts. Therefore, it is useful to know the primary freezing points of these solutions. The object of this work was to determine accurate liquidus curves for the binary system cryolite-alumina. Those previously published are in disagreement with each other, and the present and other investigators have not been able to dissolve nearly as much alumina in molten cryolite at a given temperature as the curves indicate.

The primary freezing points were determined for those parts of the system molten at 1050°C by thermal analysis and by visual examination of the cooling melt.

Materials

Hand-picked natural cryolite containing no visible impurities was crushed to pass 150 mesh. It had 0.06% loss on ignition at 700°C and contained 0.02% iron, 0.03% silicon, 0.02% magnesium, and 0.01% lead. The alumina was Linde fine abrasive alpha alumina, which had a loss on ignition at 1000°C of 0.24% and contained 0.02% sodium, 0.01% silicon, and 0.01% lead.

Apparatus

The sample was contained in a covered 10% rhodium-platinum crucible, which fitted inside an insulating firebrick box of 13 mm wall thickness. This was supported in a crucible furnace heated by a flat 80–14–6 nickel–chromium–iron resistor and lined with insulating firebrick. The platinum, 10% rhodium-platinum thermocouple was in a 5 mm protection tube, also of 10% rhodium-platinum. This alloy was used for the stirrer as well, in preference to pure platinum, because of its greater rigidity. The light beam of an arc lamp was directed into the crucible, and the melt was observed through a telescope with a magnification of twenty diameters.

A controller, used when taking cooling curves, regulated the furnace temperature so as to maintain a constant differential thermocouple voltage across the wall of the refractory box. This device (1) gives a nearly constant heat loss from the crucible and sharper arrests in the cooling curve. The controller was of the proportional position type with a continuously variable transformer to supply the furnace transformer. When the furnace temperature became too high, the power input was stepped down 15%, then reduced gradually; when it became too low, the reverse took place. An on-off controller maintained the furnace temperature for melting the sample, and, with periodic manual settings, gave the very slow rates of cooling required for the determination of primary freezing points by the visual method.

The cold junction of the measuring thermocouple was in cracked ice in a vacuum flask, and it was connected to a Rubicon Type B potentiometer. A special recorder, also supplied by the Rubicon Company, Philadelphia, registered the difference between the thermocouple output and a suitable voltage set on the potentiometer. This difference, usually in the 200 μv range, was multiplied to an appropriate level for a modified Brown Electronik strip-chart recorder by means of an external conversion unit. The balancing mechanism of this recorder was actuated by the amplifier of a photoelectric galvanometer in the microvolt circuit. The conversion unit had six ranges of 0–20 to 0–1000 μv and included a potentiometer with a range of −10 to +10 μv for testing and compensation of thermal emf's.

Method

The 150 g samples were made up by weight and heated at 1050° or 1100°C with stirring until a clear

[1] Manuscript received May 31, 1955. This paper was prepared for delivery before the Cincinnati Meeting, May 1 to 5, 1955.

[2] Present address: National Research Corporation, Cambridge, Mass.

melt was obtained. Then, for alumina contents up to 10% by weight, the melt was cooled with stirring at the rate of 1–3°C/min, and the primary freezing point determined from the cooling curve. Supercooling of up to 5°C took place. The cooling melts were observed through the telescope, and the first appearance of crystals corresponded with the primary break in the cooling curve.

For alumina contents higher than 10% there was no break in the cooling curve corresponding with the first appearance of crystals in the melt, and the primary break occurred at an appreciably lower temperature. This behavior is attributed to the sluggishness with which the crystals form and to the steepness of the liquidus curve. In this range the temperature at which crystals first appeared was taken as the primary freezing point. To minimize the effect of slow crystallization, final determinations by this visual method were made with cooling rates of less than 0.1°C/min.

The thermocouples were checked regularly at the freezing point of reagent-grade sodium chloride. This was found to be 801° ± 0.5°C using a thermocouple calibrated in pure silver and in samples of aluminum and copper certified by the National Bureau of Standards. The calibration was made in pure alumina crucibles using pure alumina thermocouple protection tubes and carbon powder over the molten metal.

Results

The freezing point of the cryolite, determined with a calibrated thermocouple, was found to be 1009° ± 1°C. Molten cryolite is slightly unstable, and on holding in the covered crucible for four hours at 1050°C, the freezing point decreased one degree.

Results for the system cryolite-alumina are shown graphically in Fig. 1 along with those of some of the investigations previously reported. The eutectic point is at 962°C and 10% alumina (weight per cent). The liquidus curve on the alumina side rises steeply to 1050°C at 16% alumina. The primary crystals which form on the alumina side of the eutectic point are hexagonal, but it was not definitely established that they are alpha alumina. Results on the cryolite side of the eutectic point, which were obtained by the cooling curve method, are not in error by more than 2°C. The limit of error on the alumina side, where the visual method was used, is estimated to be 5°C; the results will tend to be low because it is not possible to make a correction for supercooling with this method. Duplicate results by a skilled observer did not differ by more than 2 or 3°C. When a clear melt 2 or 3°C above its primary freezing point was seeded with alpha alumina, crystallization did not begin, nor did the added crystals dissolve. The loss

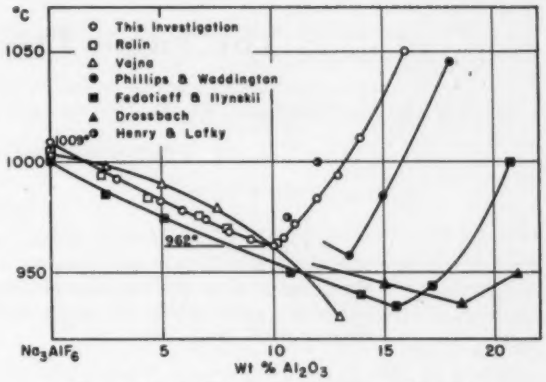

FIG. 1. Liquidus diagram for cryolite-alumina

in weight by evaporation from a melt containing 14% alumina was 1% after seven hours at 1050°C.

Rolin's data (2), which extend only to 10% alumina, do not differ from those of the present investigation by more than 3°C, while others differ by up to 10°C in this range. Above 10% alumina, the nearest other results are those of Henry and Lafky (3), who determined the percentage of alumina which would dissolve in cryolite on prolonged stirring at a given temperature. Phillips and Waddington used the cooling curve method, with a rate of 2°C/min, and observed that crystals formed in the melt before the primary break occurred. Their data, briefly reported in the discussion of Vajna's paper (4), and those of Henry and Lafky, became available after the present investigation was made. There are still greater differences between the present results and those of Fedotieff and Ilynskii (5), Drossbach (6), and other earlier investigators. They used the cooling curve method with higher rates of cooling. This method has been shown to be inadequate on the alumina side of the eutectic point.

Acknowledgment

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1956 JOURNAL.

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The Vapor Pressure of Rhenium[1]

E. M. Sherwood, D. M. Rosenbaum, J. M. Blocher, Jr., and I. E. Campbell

Battelle Memorial Institute, Columbus, Ohio

ABSTRACT

The vapor pressure of rhenium was determined over a temperature range of 2220°–2725°C. At 2500°C, the vapor pressure of rhenium is approximately one and one-half times that of tantalum. Estimates were made of the boiling point of rhenium (5630°C) and of the vapor pressure of liquid rhenium. The computed ΔH_s° of sublimation of rhenium is 187 kcal.

Introduction

Rhenium, with a melting point of 3180°C and a density of 21, is a relatively rare and quite expensive metal which, nevertheless, offers attractive possibilities as a material for electronic and other specialized applications. Its high resistance to attack in the so-called "water cycle" (hundreds of times better than tungsten, under certain conditions) (1) is of particular advantage in electron-tube applications. However, in order to evaluate fully the potential importance of rhenium in such a field of use, it was desirable to have information concerning its vapor pressure.

To obtain the required information, the Langmuir weight-loss method, which has been used previously in determining the vapor pressure of such metals as titanium (2), was employed. The validity of the data was checked by thermodynamic calculations, and both the boiling point of the metal and the vapor pressure of liquid metal were estimated.

Description of the Test Method

The Langmuir weight-loss method (3) involves heating a wire of the desired material in a good vacuum (10^{-5} mm Hg, or less) at a constant temperature, for a measured time interval, and determining the loss in weight as a result of evaporation of metal from the wire. The following relationships, (I) and (II), are then used to compute the vapor pressure.

$$\log p_{atm} = \log m - \tfrac{1}{2} \log M + \tfrac{1}{2} \log T - 1.647 \quad \text{(I)}$$

where p_{atm} = vapor pressure, atmospheres,[2] M = gram molecular weight of the vapor, T = temperature, degrees Kelvin, and m = rate of evaporation, g/cm²/sec.

$$\text{Further,} \quad m = \left(\frac{\rho}{\pi}\right)^{1/2} \cdot \left(\frac{W_o^{1/2} - W^{1/2}}{t}\right) \quad \text{(II)}$$

where ρ = computed density at temperature of run, g/cc, W_o = initial weight/unit length of wire, g/cm, W = final weight/unit length of wire, g/cm, and t = time of run, sec.

Test Specimens

The specimens used in the experimental work were in the form of wires, about 0.050 in. in diameter by 6 in. long. These wires were made by cold pressing minus 325-mesh rhenium powder at 30 tons/in.² into the form of bars ¼ x ¼ x 6 in. in size. Stearic acid in ether was used as a die lubricant. The density of the pressed bars was 35–40% of the theoretical value. The bars were presintered in a vacuum of 10^{-6} mm Hg for 2 hr at 1200°C to improve their strength. A 5% increase in density was secured at this step. Subsequent sintering of the bars in hydrogen at 2700°C for 1 hr produced densities 85–93% of theoretical.

The following fabrication schedule was used, with appropriate intermediate anneals in hydrogen for 2 hr at 1750°C: (*a*) careful hand hammering of corners of bars; (*b*) cold rolling of the corners to produce bars of octagonal cross section; (*c*) cold swaging, at 20% reduction per pass, until the diameter was reduced to 0.060 in.; (*d*) cold wire drawing, at 10% reduction, to the finished size of approximately 0.050 in.

Fig. 1 is a photomicrograph of a longitudinal section of a typical wire specimen in its condition prior to test.

Test Equipment

The test specimen was supported in a horizontal position by two split molybdenum clamping blocks, each 0.5 in. in diameter by 1.5 in. long. Each of these blocks was provided with a tapped hole so that it could be screwed onto the 0.25-in. diameter tungsten supporting electrode. This assembly was mounted in a 100-mm Pyrex bulb with the ends of the tungsten electrodes protruding from the bulb and sealed to it by uranium glass (Fig. 2).

A 45-mm Pyrex tube, with an optically flat Pyrex

[1] Manuscript received April 11, 1955.

[2] Strictly, $\alpha \cdot p_{atm} = m \cdot \text{const} \cdot T^{1/2} \cdot M^{1/2}$, the familiar Knudsen equation. As is usually valid for metals, α, the accommodation coefficient, is assumed equal to unity (4).

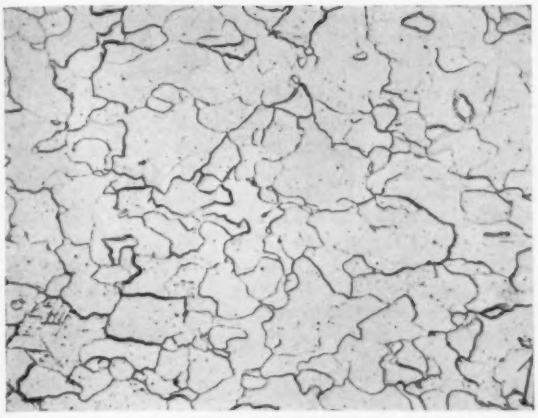

FIG. 1. Longitudinal section of typical rhenium-wire specimen (250 magnification, electrolytic oxalic acid etch).

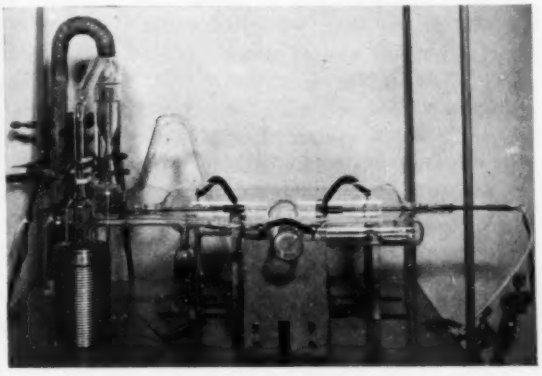

FIG. 2. Experimental equipment

plate sealed in its free end, was joined at right angles to the bulb, and perpendicular to the test specimen at its center. The temperature of the wire was determined by a L&N optical pyrometer, which had been calibrated, with the flat Pyrex sight window in place, against a N.B.S. standard tungsten-ribbon lamp. The observed temperatures (accuracy of observation about ±10°K) were corrected for the emissivity of rhenium. Over the temperature range used in these determinations (2500°–3000°K), the emissivity at 0.655 μ varies between 0.39 and 0.36. The "true" temperature was obtained from a previously determined[3] calibration curve showing the relation between black-body temperature and brightness temperature for rhenium. A magnetically operated glass shutter was placed in the line of sight between the test wire and the optical window to prevent condensation of evaporated rhenium on the window. The shutter was maintained in this position except when temperature determinations were being made.

[3] Unpublished work at Battelle Memorial Institute.

Fig. 2 illustrates the complete vacuum system (except for the mechanical fore pump), which includes an ionization gauge, liquid-nitrogen trap, and three-stage mercury diffusion pump.

In all test runs the pressure was less than 10^{-5} mm of Hg.

Procedure

With the specimen in place, the system was evacuated to about 10^{-5} mm and then filled with high-purity helium as a purge. Next, the system was re-evacuated to 10^{-5} mm, or lower, and the rhenium was electrically heated, with stabilized a-c power, to the desired temperature as rapidly as possible. Wire temperature was maintained constant by adjusting the applied voltage so that the product of the cube root of the current and the voltage was constant. Test runs were terminated when it was judged that sufficient metal had been evaporated from the surface of the wire to permit accurate weight-loss determination.

RESULTS

Table I lists the results of the experiments. High temperature densities, calculated from extrapolated linear coefficient of thermal expansion data,[3] were used in equation (II). Density values ranged from 19.73 to 19.93 g/cc. Owing to the cooling effect of the molybdenum clamping blocks, a sharp temperature gradient existed adjacent to the blocks. To compensate for this gradient, an effective wire length, ½ in. less than the free length of the wire between the blocks, was used in the computations.

An empirical expression for the vapor pressure of rhenium was calculated from the experimental determinations, using the method of least squares. For the temperature range covered, equation (III) is a valid representation of the vapor pressure of rhenium:

$$\log_{10} p_{\text{atm}} = 7.5237 - 40865/T \qquad \text{(III)}$$

or

$$\log_{10} p_{\text{mm}} = 10.4038 - 40865/T$$

TABLE I. *Experimental values of vapor pressure for rhenium*

Corrected temperature		Duration of run, sec	Rate of evaporation, g/cm²/sec	Vapor pressure	
°C	°K			Atmosphere	mm Hg
2221	2494	259,200	1.54×10^{-8}	1.24×10^{-9}	9.39×10^{-7}
2250	2523	151,200	3.23×10^{-8}	2.61×10^{-9}	1.98×10^{-6}
2332	2650	30,600	7.35×10^{-8}	6.04×10^{-9}	4.59×10^{-6}
2475	2748	54,000	6.96×10^{-7}	5.56×10^{-8}	4.23×10^{-5}
2480	2753	23,400	4.67×10^{-7}	3.93×10^{-8}	2.99×10^{-5}
2606	2879	7,200	2.77×10^{-6}	2.38×10^{-7}	1.81×10^{-4}
2726	2999	1,560	8.41×10^{-6}	7.37×10^{-7}	5.60×10^{-4}

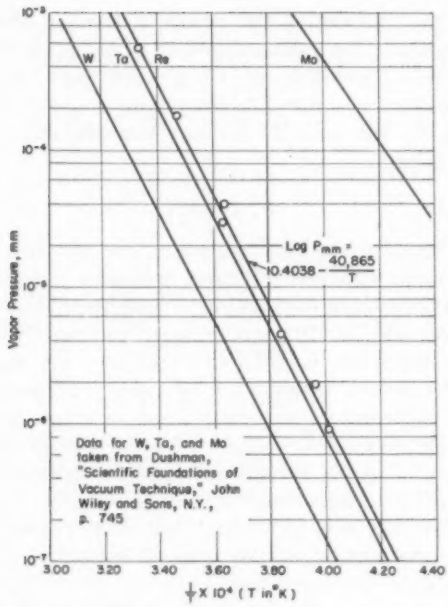

FIG. 3. Vapor pressure of rhenium and other refractory metals as a function of reciprocal temperature.

The vapor pressure of rhenium, so determined, is about ten times greater than that of tungsten and about one and one-half that of tantalum. This is illustrated in Fig. 3, in which data for molybdenum are given as well.

Thermodynamic Treatment

The following important relationship forms the basis for the thermodynamic calculations presented in this section:

$$-R \ln p_{atm} = [(F^\circ - H^\circ_o)/T]_g - [(F^\circ - H^\circ_o)/T]_{c,l} + \Delta H^\circ_o/T,$$
$$= \Delta[(F^\circ - H^\circ_o)/T] + \Delta H^\circ_o/T \qquad \text{(IV)}$$

where R = the universal gas constant, 1.987 cal/mole, $[(F^\circ - H^\circ_o)/T]_g$ = the free-energy function for the vapor, $[(F^\circ - H^\circ_o)/T]_{c,l}$ = the free-energy function for liquids or crystalline solids, ΔH°_o = the heat of sublimation at absolute zero, in cal/mole.

$$\Delta[(F^\circ - H^\circ_o)/T] = [(F^\circ - H^\circ_o)/T]_g - [(F^\circ - H^\circ_o)/T]_{c,l} \qquad \text{(V)}$$

$[(F^\circ - H^\circ_o)/T]_g$ can be determined from spectroscopic data, $[(F^\circ - H^\circ_o)/T]_{c,l}$ can be evaluated when the thermal variation of C_p, the heat capacity, is known and appropriate account is taken of phase changes.

The source of the spectroscopic data used in the calculation of the free-energy function for rhenium vapor was Klinkenberg (6).

TABLE II. ΔH°_o *of sublimation for rhenium*

T, °K	$-\left[(F^\circ - H^\circ_o)/T\right]_g$	$-\left[(F^\circ - H^\circ_o)/T\right]_c$	Vapor pressure, atm	ΔH°_o, cal
2494	50.735	16.172	1.24×10^{-9}	187,826
2523	50.793	16.254	2.61×10^{-9}	186,218
2605	50.953	16.481	6.04×10^{-9}	188,013
2748	51.222	16.865	5.56×10^{-8}	185,622
2753	51.231	16.878	3.93×10^{-8}	187,848
2879	51.458	17.203	2.38×10^{-7}	185,860
2999	51.670	17.505	7.37×10^{-7}	186,601
Average				186,855 ±1015

The thermal variation of the specific heat of rhenium from 0° to 300°K was computed using Seitz (7).

Since this paper was presented, Cobble, Oliver, and Smith (8) have presented experimental data for C_p over this temperature range. The computed values used in this work are only a few per cent lower than those of the above published work.

The data of Jaeger and Rosenbohm (9) were used over the range 300°–1500°K, and were extrapolated to the melting point.

A discontinuous increase in C_p of 0.9 cal/mole/° was assumed at the melting point. The heat capacity for liquid rhenium was assumed constant up to the boiling point.

Vapor pressure of the solid.—Equation (IV) was used first to assess the quantitative accuracy of the experimental data; i.e., ΔH°_o was computed for each of the experimental temperatures, using the corresponding measured values of the vapor pressure. Table II lists the results of these computations. Although the standard deviation from the mean is 1015 calories, somewhat higher than might be desired, no over-all trend upward or downward is indicated. The value 187,000 calories has been taken as ΔH°_o of sublimation for rhenium.

Next, $\Delta[(F^\circ - H^\circ_o)/T]$ was expanded as a quadratic function of T over the range of experimental data, using the values for $\Delta[(F^\circ - H^\circ_o)/T]$ from Table II and at the melting point, i.e.,

$$\Delta[(F^\circ - H^\circ_o)/T] = a + bT + cT^2 \qquad \text{(V)}$$
$$= -37.327 + 14.258 \times 10^{-4} T - 1.257 \times 10^{-7} T^2$$

Equation (IV) becomes

$$-R \ln p_{atm} = -37.327 + 14.528 \times 10^{-4} T - 1.257 \times 10^{-7} T^2 + 187{,}000/T$$
$$-\log p_{atm} = (1/4.5753) \cdot (-37.327 + 14.258 \times 10^{-4} T - 1.257 \times 10^{-7} T^2 + 187{,}000/T) \qquad \text{(VI)}$$

TABLE III. *Vapor pressure of liquid rhenium*

T, °K	$-[(F_o - H^o_o)/T]$	Computed vapor pressure of liquid rhenium, atm
3453 (mp)	33.846	3.64×10^{-5}
3500	33.784	5.09×10^{-5}
4000	33.177	1.08×10^{-3}
4500	32.663	1.14×10^{-2}
5000	32.238	7.44×10^{-2}
5500	31.906	0.349
5900 (bp)*	31.702	1.000

* (mp) = melting point; (bp) = boiling point.

The vapor pressure of solid rhenium then can be calculated from equation (VI) for the experimental temperatures.

Vapor-pressure values, determined experimentally, were compared with those calculated from both equation (III) and equation (VI). In general, good agreement was obtained in both cases, the average difference between experimental and calculated values being about 16%. For the highest temperature at which tests were run (2999°K), equation (III) failed to give a good approximation, and the calculated value was too high. Further departure of the values computed using equation (III) from those made using equation (VI) occurred at still higher temperatures. However, it should be noted that the value of the vapor pressure at the melting point (3.83×10^{-5} atm), calculated using equation (VI), was quite close to the value obtained using equation (VII) (3.64×10^{-5} atm).

Vapor pressure of liquid rhenium.—After a reasonable value for ΔH^o_o was obtained, equation (IV) was used to compute the vapor pressure of liquid rhenium at various temperatures above the melting point. These computed values are, in reality, estimates, since no data are available for the heat capacity of liquid rhenium. Brewer (10) has estimated the entropy of fusion of rhenium as 2.3 eu, and this value was used in computation of the free energy function of liquid rhenium, above the melting point (3180°C). The heat capacity of liquid rhenium was assumed to be 10.8 cal/mole/°. As was done for the solid, $\Delta[(F^o - H^o_o)/T]$ was expanded as a function of T from the melting point upward to give:

$$\Delta[(F_o - H^o_o)/T] = -40.582 + 25.807 \times 10^{-4}T - 1.824 \times 10^{-7}T^2 \quad \text{(VII)}$$

Using equations (IV) and (VII), the values of Table III were computed.

If p_{atm} is set = 1 in equation (IV), then its logarithm is zero, and, by a method of successive approximation, T_{bp} can be calculated. The value so obtained is 5900°K (5630°C), as indicated in the table.

Discussion of Results

The reliability of the data appears to be good. The chief source of possible error lies in the assumption that the temperature of the wire test specimen was uniform except for about ¼ in. at each end near the clamping electrodes.

Measurement of temperature variation over the length of the resistively heated specimen indicates that the effective length adopted was accurate to within 10%.

The absence of volatile impurities was evidenced by the fact that runs made at successively lower temperatures with the same wire checked runs made at successively higher temperatures.

No evidence of metal-film formation was detected on the sight-window, indicating that the glass shutter performed satisfactorily.

Lack of information on the heat capacity of rhenium from about 1200°C to the boiling point offered the most serious handicap in arriving at good estimates of the boiling point of rhenium and the vapor pressure of liquid rhenium. Since these estimates were made (11), tests have been run, over the temperature range 1500°–2700°K, which indicate both the manner in which C_p for rhenium varies and the relative value of C_p for rhenium compared to that for tungsten. It is believed that estimated values in this temperature range are within less than 10% of the true values. For example, the recently measured value of C_p at 2700°K was about 9.5 cal/mole/°, whereas the assumed value was about 9.1 cal/mole/°.

Finally, still better estimates of the vapor pressure of liquid rhenium and of the boiling point could have been made if experimental data on the heat of fusion of rhenium were available.

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1956 Journal.

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The Kinetics of Formation of Anodic Ta_2O_5—Further Studies[1]

D. A. Vermilyea

General Electric Research Laboratory, Schenectady, New York

ABSTRACT

A new investigation of the kinetics of formation of anodic Ta_2O_5 films showed that data reported previously are in error. The new data show that the activation energy for the process is not a single linear function of the applied electric field, and that the pre-exponential factor is also a function of the applied field. Possible mechanisms are considered, but none explains the results adequately.

Introduction

In a previous paper (1) data obtained from measurements of the growth of anodic oxide films on tantalum were presented. It was found possible to describe the data by an equation of the type

$$\dot{X} = A \exp (BE - Q/kT) \qquad (I)$$

where $\dot{X}$ is the rate of film growth, A and B are constants, E is the electric field strength, and Q is an experimental activation energy. More extensive measurements with improved techniques suggest a better interpretation of the data. This paper presents the results of these recent measurements.

Experimental

All of the equipment used, which consisted of a constant voltage power supply, constant temperature bath, an automatic timing circuit, and a calibrated optical step gauge for measuring thickness, were described previously (1). The absolute accuracy of the step gauge was checked by a direct measurement of film thickness (see Appendix), and thicknesses measured with the step gauge were found to be within at least 10% of the true thickness.

In the previous paper the major emphasis was placed on experiments conducted with a constant current power supply. The range of electric field strengths available by this method is limited by the long times required at very low currents and by heating of the specimen at high currents. On the other hand, when constant voltage experiments were made it was necessary to correct the recorded times because it was not possible to start with zero film thickness at zero time. The correction for initial conditions involved an extrapolation, and errors were introduced because of the short total time range over which the extrapolation was made. In addition, it is now known that polarization at the cathode was overcompensated for in the first constant voltage experiments.

In the experiments reported in the present paper only the constant voltage method was used. A small cathode of about 0.5 cm^2 was used so that cathode polarization would always reach its maximum value in a time which was shorter by a factor of at least 10^2 than the time of voltage application. In the earlier experiments a large cathode prevented the polarization from rising quickly enough. All of the experiments were conducted using 2% nitric acid for the electrolyte and a constant voltage of 100 volts.[2]

The method of obtaining data was as follows. An oxide film was formed on the specimen to a thickness such that about 250 ma would be passed through the cell when 100 v was applied at the desired temperature. The voltage drop due to polarization plus resistance in the cell was measured at 250 ma using a platinum anode, and the value obtained was added to 100 v. This total voltage was then applied to the tantalum for 0.1 sec, after which the specimen was removed and the oxide film thickness measured. This process was repeated, using longer time intervals as the current decreased, corrections for polarization and resistive voltage drops being made for each expected current.

Once the data were obtained, plots were made of thickness vs. the logarithm of the time. On these plots the original thickness was included by adding 0.1 sec to all measured times. Next, several electric field strengths were selected and the thickness at each field calculated; the rate of film growth at that thickness was obtained for each temperature by dividing the slope of the appropriate thickness vs. log time plot by the time required to reach that thickness. Activation energies were then obtained by the method of least squares for each field strength selected.

[1] Manuscript received September 22, 1954. This paper was prepared for delivery at the Cincinnati Meeting, May 1 to 5, 1955.

[2] 100 volts is the true voltage after correction for reaction voltage as described in reference (1).

Results and Discussion

Fig. 1 and 2 show thickness vs. log time plots for 0° and 99°C, respectively. The curve for 0°C is linear to about 4×10^5 sec, while the curve for 99°C is nowhere linear. Intermediate temperatures give plots which varied gradually from nearly all linear at lower temperatures to nearly all curved at higher temperatures. Fig. 3 shows a plot of activation energy vs. electric field strength, while Fig. 4 shows the variation with field strength of the intercepts at $T = 0°K$ of the activation energy plots.

Fig. 5 shows plots of the data obtained in the present investigation and in the earlier investigation at 19°C as well as a replot of data reported by Young (2) from experiments at 20°C. Earlier data obtained from constant current experiments agree well at low fields with the later data obtained from

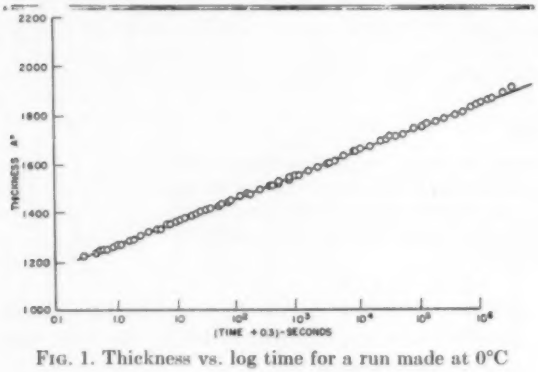

Fig. 1. Thickness vs. log time for a run made at 0°C

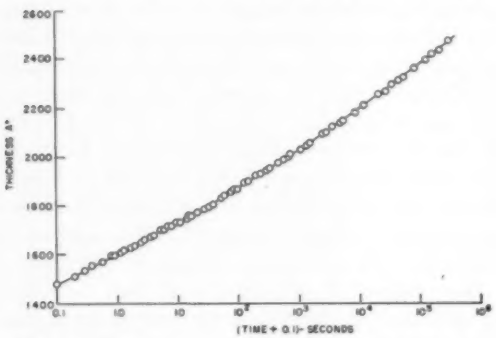

Fig. 2. Thickness vs. log time for a run made at 99°C

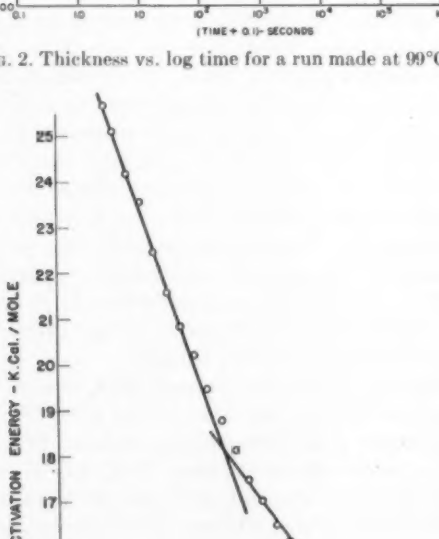

Fig. 3. Activation energy as a function of applied field

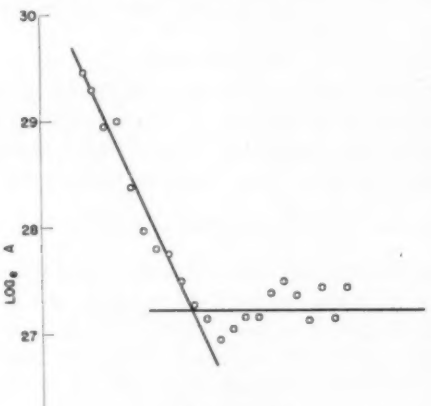

Fig. 4. Pre-exponential factor as a function of applied field.

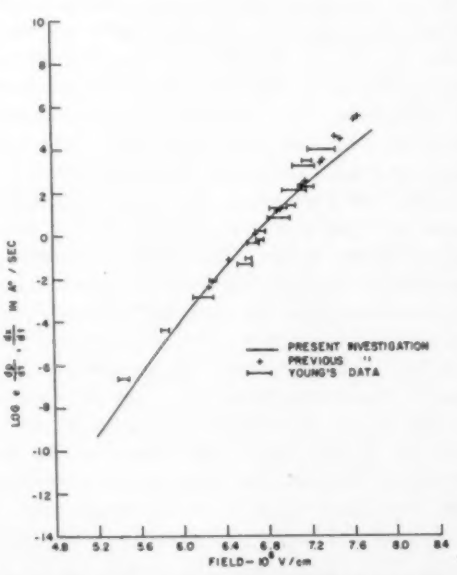

Fig. 5. Log rate as a function of applied field for this and previous investigations.

constant voltage experiments, but, at high fields, rates of film growth at a given field are greater in earlier data. It is believed that this discrepancy results from heating the oxide film above the bath temperature in the earlier experiments. In the previous paper a calculation was made of the temperature rise which a specimen would undergo when a specific current density was passed for a few seconds, and it was found that the expected temperature rise was a few degrees centigrade. The estimated temperature rise was probably low, because the boundary conditions, which assumed constant rate of heat input to one face of an infinite piece of metal, were not exactly those of the experiment. It would be difficult to make an exact calculation of the actual temperature rise which occurred in the earlier experiments, but it was certainly enough to influence the results seriously. In the present investigation, where at high current densities the time of voltage application was only 0.1 sec, such heating was negligible.

It may be seen from Fig. 5 that the data reported by Young agree well with the earlier data obtained by Vermilyea (1). Young employed a constant current method for obtaining data, and his results were also probably influenced by heating the specimen at high formation rates.

According to the mechanism proposed by Mott and Cabrera (3), a plot of activation energy vs. applied field should give a straight line of slope $q\lambda/kT$, where q is the charge on the diffusing ion and λ is the distance from the position of equilibrium in the metal to the top of the energy barrier opposing entrance into the oxide. This mechanism assumes that the rate-controlling step consists of moving an ion from the metal into the oxide, and that once the ion is in the oxide it moves rapidly to the outer interface and reacts to form oxide.

It is apparent from Fig. 3 that one straight line cannot be drawn through the points, but two straight lines seem to fit the data fairly well except for a transition region. At the present time no mechanism which accounts satisfactorily for this behavior has been found. One plausible hypothesis which was examined proposed that the curve of Fig. 3 resulted from the presence of two successive barriers to the motion of ions, one effective at low and one at high electric fields. Evidence presented in a previous publication (4) indicates that tantalum is the mobile ion during anodic oxidation. If it is assumed that the charge on the tantalum is +5, the heights of the two barriers in the absence of an applied field would be 2.17 and 1.47 electron volts, while the corresponding half widths would be 4.8 Å and 2.4 Å. The larger barrier might be thought to be the one at the metal-oxide interface with the smaller one opposing motion within the film.

One difficulty with such a proposal is that, at high fields when the controlling step is within the film, a space charge would develop which would result in a nonuniform field. Dewald (5) has suggested that space charges may be important in determining the kinetics of anodic oxidation, but it has been shown (6) that any space charge must be very small. There is the possibility, however, that any space charge formed in the film might be negligible except at the metal-oxide interface, so that the field in the oxide film might be linear except for a small boundary layer. That this is *not* a possible explanation of the observed results may be shown as follows. Consider a constant current experiment conducted at constant temperature. The flux of ions past the metal-oxide interface is given by

$$J_I = C_I A_I \exp^{-\Delta H_I/kT} \exp^{q\lambda_I E_I/kT} \qquad \text{(II)}$$

while at any plane in the oxide a distance X from the interface the flux will be

$$J_X = C_X A_X \exp^{-\Delta H_X/kT} \exp^{q\lambda_X E_X/kT} \qquad \text{(III)}$$

where C_I, C_X = concentration of diffusing species at the metal-oxide interface and in the film, respectively. A_I, A_X = frequency factors at the interface and in the film. These frequency factors consist of the product of a vibrational frequency, an entropy of activation, and a lattice constant. ΔH_I, ΔH_X = heats of activation at the interface and in the oxide. q = charge on diffusing ion. λ_I, λ_X = half widths of the barriers opposing diffusion at the interface and in the oxide. E_I, E_X = electric field intensity at the interface and in the oxide. ΔH_X, λ_X, and A_X are assumed to be constant throughout the film. Assuming that the fluxes are divergence free,

$$J_I = J_X \qquad \text{(IV)}$$

The concentration of ions at any plane is therefore:

$$C_X = \frac{C_I A_I \exp(-\Delta H_I/kT) \exp q\lambda_I E_I/kT}{A_X \exp(-\Delta H_X/kT) \exp q\lambda_X E_X/kT} \qquad \text{(V)}$$

$$= B \exp q/kT(\lambda_I E_I - \lambda_X E_X)$$

where B is a constant at any one temperature. Poisson's equation for one-dimension states that

$$\frac{dE}{dX} = \frac{4\pi\rho}{\kappa} \qquad \text{(VI)}$$

where ρ is the charge density and κ is the dielectric constant. Substituting the value of C_X from equation (V) in equation (VI) gives:

$$\exp\left(\frac{q\lambda_X}{kT} E_X\right) dE = \left(\frac{4\pi ze}{\kappa}\right) B \exp\left(\frac{q\lambda_I}{kT} E_I\right) dX \qquad \text{(VII)}$$

TABLE I. *Calculated field as a function of distance in the film*

X = distance from oxide-metal interface	Field	Average field in a film of thickness X
Å	v/Å	v/Å
0	0.0626	—
100	0.0629	0.0627
500	0.0635	0.0631
1000	0.0642	0.0635
1500	0.0648	0.0639
2000	0.0654	0.0642
3000	0.066	0.0647
4000	0.0665	0.0651
5000	0.0669	0.0654

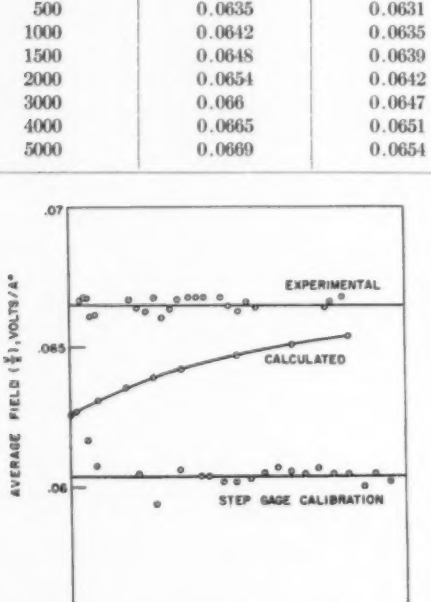

FIG. 6. Average field vs. film thickness. The calculated and experimental values are for anodization at 0.815 Å/sec at 19°C.

where z = the valence of the diffusing ion, and e = the electronic charge. Integrating and solving for E_X gives:

$$E_X = \frac{kT}{q\lambda_X} \ln \left\{ \frac{q\lambda_X}{kT} \cdot \left[\frac{4\pi ze}{\kappa} B \exp\left(\frac{q\lambda_I E_I}{kT}\right) X + D \right] \right\} \quad \text{(VIII)}$$

where D is a constant of integration. Solving for D subject to the boundary condition $E_X = E_I$ at $X = 0$, and substituting again in equation (VIII), the final expression for E_X is:

$$E_X = \frac{kT}{q\lambda_X} \ln \left[\frac{q\lambda_X}{kT} \frac{4\pi ze B}{\kappa} \exp\left(\frac{q\lambda_I E_I}{kT}\right) X + \exp\left(\frac{q\lambda_X E_I}{kT}\right) \right] \quad \text{(IX)}$$

In order to calculate E_X as a function of distance in the film it is necessary to evaluate the constant B, which involves some assumptions regarding vibrational frequency and entropy of activation. It will be assumed that the vibrational frequency is 10^{13} and that the entropy of activation is 20 cal/degree. These values are both probably somewhat too large. They were deliberately chosen in this way to minimize the concentration of ions in transit required to give the observed pre-exponential factor. If the resultant space charge distorts the field in the film too much when the concentration is low, it may be concluded that the mechanism is invalid.

From Fig. 4, the pre-exponential factor at fields in which control is assumed to be in the film is 6×10^{11}, if the growth rate, $\dot{X}$, is expressed in Å/second, and it will be assumed that the value is the same for processes in the film and at the interface. The ion flux $C_I A_I$ corresponding to 6×10^{11} Å/sec is 1.43×10^{26} ions/cm²/sec. The quantity A_x is given by $2\lambda_x \nu \exp(\Delta S/R)$, where ν is the vibration frequency. Taking $2\lambda_x = 4.76 \times 10^{-8}$ from Fig. 3, $A_x = 1.114 \times 10^{10}$. Using the values for heats of activation at zero field obtained from Fig. 3, $B = 7.9 \times 10^{-3}$ at $T = 19$°C.

Consider now a constant-current experiment conducted at 19°C and a rate of 0.815 Å/sec. The field required at the metal-oxide interface to produce an ion flux equivalent to this rate is found from the data in Fig. 3 to be 6.26×10^6 v/cm. Using this value for E_I, assuming $q = 5$, $K = 25$, and taking $\lambda_I = 4.8$ Å, E_X was calculated for different values of X with the results shown in Table I. From a plot of field vs. thickness, the average field was calculated by graphical integration, and these values are also included in Table I.

The increase in average field thickness is about 4% over the thickness range from 100 to 5000 Å. In order to determine whether such an increase actually occurs, a specimen was anodized under the conditions for which the calculation was made, the thickness and voltage being measured periodically. The average field at each thickness was then calculated by dividing the voltage by the thickness.[3] Fig. 6 shows a plot of the calculated and experimental values of the average field for these conditions. It may be seen that the experimental field is constant with thickness, and that the increase in the calculated field is large compared to the experimental uncertainty. Also, the calculated fields are less than the experimental fields at all thicknesses.

Since the thicknesses were measured by comparison with the optical thickness step gauge, it was necessary to be certain that there was no com-

[3] The applied voltage must be corrected for the voltage of the electrochemical reaction (7).

pensating error in the step gauge. The data of Fig. 4, reference (1), are replotted in Fig. 6 to show that the average field in the specimens used to calibrate the step gauge does not change with film thickness. The scatter at small thicknesses is a result of the poorer sensitivity of the measurement for thinner films.

It is concluded on the basis of these calculations that the observed results are not to be explained on the basis of the two postulated energy barriers. Another possible explanation of the observed results is that the field changes the activation energy by changing the nature of the film. It has been observed that the dielectric constant of the film and the rate of solution of the film in hydrofluoric acid are functions of the formation field, and perhaps the activation energy for ion movement is also. An investigation of these effects is now in progress.

Conclusions

1. The activation energy for the rate-determining step during anodic oxidation of tantalum is not a single linear function of the applied electric field.

2. The pre-exponential factor in the equation for the rate of growth of the film is a function of the applied electric field. The factor is nearly constant above a certain field but increases at lower fields.

3. Because the accumulation of a space charge in the oxide film results in nonlinearity of the thickness-voltage plot at constant formation rate while such plots are actually linear, mechanisms involving the accumulation of large space charges in the film are not in agreement with experiment.

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Appendix

A measurement of the true thickness of an oxide film was made by stripping the film from the metal, mounting a very small flake of the film in the electron microscope, turning the flake until it was as nearly as possible parallel to the electron beam as evidenced by the smallest possible shadow on the fluorescent screen, and measuring the width of the resulting shadow. A film which was estimated to be 5000 Å thick by comparison with the optical step gauge was found by the electron microscope method to be 5200 Å ± 250 Å. The agreement is very good, especially when it is considered that the measurement with the electron microscope would tend to be slightly high because of charging of the flake by the electron beam.

Technical Note

Surface Contamination of Copper by Phosphate Ion During Electropolishing—Use of P^{32} *

N. H. Simpson[1] and Norman Hackerman

Department of Chemistry, University of Texas, Austin, Texas

In the course of an investigation on surface migration of copper ion on the surface of single crystals of copper it was necessary to electropolish. This was done in a phosphate bath and it was desirable to know whether the surface retained any of the phosphate.

Both single crystal copper and polycrystalline copper specimens were used. Work hardened material was removed by etching in 20% nitric acid and the specimens were then hand polished (holding them with soft paper tissue) with No. 2, 3, and 4 metallographic emery paper in succession. The paper was laid on plate glass. Polishing[2] was carried out by stroking in a given direction until all markings ran in the same direction. The specimen was then rotated 90° and the process was repeated. Grit particles were removed from the surface, between each type of emery paper used, with soft paper tissue.

After mechanical polishing, a piece of copper wire was wound around the crystal to serve as a means of handling the specimen thereafter. Loose particles were again removed from the surface with soft tissue and the specimen was then rinsed in distilled water, in ethyl alcohol, and in ether to remove both grease and water soluble contaminants. This process was then reversed, with the final rinse in distilled water. All specimens were repolished between experiments.

The specimen was then suspended in a solution made of equal volumes of 85% H_3PO_4 (analytically pure) and distilled water. The solution was preelectrolyzed between copper electrodes. This "ageing" step was necessary since its omission led to nonuniform polishing and to pitting. Probably the step raises the copper ion activity in solution and this, in turn, increases the dissolution potential enough so that copper dissolves more rapidly on the raised portions of the surface.

The specimen to be polished was made the anode in the solution after treatment as described, and 99.90% copper sheet served as the cathode. Approximately one volt was applied across the cell, and a current of approximately one ampere flowed. The voltage was maintained low enough to prevent formation of gas bubbles on the specimen since pits formed beneath them. If bubbles did form the specimen was removed, rewashed, and mechanically repolished before continuing the electropolishing. The proper polishing voltage could be maintained by keeping it within the range where a slight pulsation was apparent. This pulsation may have been caused by a monomolecular build-up of a hydrated

TABLE I. *Data from phosphate retention test*

Experiment No.	Treatment after electropolishing	Phosphate remaining, calculated as molecular layers
Polycrystalline		
1	Rinsed 5 min in tap H_2O, 5 min in dist. H_2O, room temperature	0.70
2	Rinsed 6 min 50°C tap H_2O, 4 min dist. H_2O, room temperature	0.29
Single Crystals		
3	Rinsed 6 min 50°C tap H_2O, 4 min in dist. H_2O, room temperature	0.14
4	Rinsed 6 min in 19°C tap H_2O, 4 min in dist. H_2O	1.20
5	Rinsed 10 min room temperature in dist. H_2O	1.20
6	Rinsed 6 min in boiling tap H_2O, 4 min in boiling dist. H_2O	<0.06
7	Rinsed 6 min in boiling tap H_2O, 4 min in boiling dist. H_2O	0.09
8	Boiling dist. H_2O for 10 min	0.35

* Manuscript received April 15, 1955.

[1] Present address: Chief, Engineering Test Laboratory, Convair, Fort Worth, Texas.

[2] The method was described in private communication with S. V. Cathcart and P. Smith of the Oak Ridge National Laboratories, Oak Ridge, Tennessee.

copper phosphate coating followed by its dissolution or sloughing off. The specimen was allowed to polish in this range for approximately 30 min. If conditions were right, an exceedingly high polish was obtained on the surface of the copper.

The amount of phosphate retained was determined by using $H_3P^{32}O_4$.[3] After distilling until a silver nitrate test showed no chloride ion the tagged phosphoric acid was diluted with 85% analytically pure H_3PO_4. Enough of the $H_3P^{32}O_4$ was used to produce a count of approximately 1×10^7/minute/μl. This solution was diluted to twice its volume with distilled water and after ageing with copper, as explained above, was used in the electropolishing experiments.

[3] Obtained from Oak Ridge National Laboratory, Isotope Division.

Data for both a polycrystalline specimen and a single crystal are given in Table I.

It is apparent that some phosphate was retained even after thorough rinsing. The amount left decreased with increasing temperature of the wash. The effect is noticeably greater for tap water than for distilled water. In fact, the amount left after treatment with boiling tap water (plus distilled water) is not significant, i.e., it is within experimental error. The more complete removal by boiling tap water, as compared to boiling distilled water, may be caused by the *p*H difference.

It was concluded that since oxidation occurs in the boiling water system, the optimum condition for removal of phosphate from polished copper surfaces is that given by experiment 3 in Table I.

Any discussion of this paper will appear in a Discussion Section to be published in the June 1956 JOURNAL.

FUTURE MEETINGS OF
The Electrochemical Society

San Francisco, April 29, 30, May 1, 2, and 3, 1956

Headquarters at the Mark-Hopkins Hotel

Sessions will be scheduled on

Electric Insulation, Electronics (including Instrumentation, Luminescence, Oxide-Cathodes, Phosphor Application, and Semiconductors), Industrial Electrolytics, Electrothermics and Metallurgy, and probably Theoretical Electrochemistry

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Cleveland, October 28, 29, 30, 31, and November 1, 1956

Headquarters at the Statler Hotel

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Washington, D. C., May 12, 13, 14, 15, and 16, 1957

Headquarters at the Statler Hotel

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Buffalo, October 6, 7, 8, 9, and 10, 1957

Headquarters at the Statler Hotel

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New York, April 27, 28, 29, 30 and May 1, 1958

Headquarters at the Statler Hotel

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Ottawa, September 29, 30, October 1, and 2, 1958

Headquarters at the Chateau Leurier

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Papers are now being solicited for the meeting to be held in San Francisco. Triplicate copies of each abstract (*not exceeding 75 words in length*) are due at the Secretary's office, 216 West 102nd Street, New York 25, N. Y., *not later than January 2, 1956* in order to be included in the program. *Indicate on abstract for which division the paper is to be scheduled.* Complete manuscripts should be sent in triplicate to the Managing Editor of the JOURNAL at the same address.